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Collection and Treatment of Wastewater Generated by Pesticide Applicators

Purdue Univ.
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16. ABSTRACT

Methods for control of pesticide contaminated wastewater were studied. Evaluation of practices that are currently used to handle pesticide contaminated wastewaters was followed by development of a system that could be used to collect the pesticide contaminated wastewaters. Then a treatment plant was developed to remove pesticide from contaminated wastewaters and produce a high-quality effluent. Three physical-chemical treatment options were evaluated. A flocculation/coagulation/sedimentation step was evaluated using alum as the coagulant. Additional studies were done using filtration and coalescence. Flocculation/coagulation/sedimentation removed a high percentage of the pesticides. The filtration and coalescence steps were less effective. The supernatant from the first step was then passed through activated carbon columns. A hydraulic loading rate of .5L/s-m^2 was determined to be adequate with a residence time of approximately 15 minutes. The concentration of the pesticides in the clear effluent was usually less than 1 mg/liter.

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COLLECTION AND TREATMENT OF WASTEWATER GENERATED BY PESTICIDE APPLICATORS

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

Pesticide contaminated wastewater presets a threat to the environment when it is dumped after the cleanup of application equipment. A coagulation/flocculation/sedimentation process followed by activited carbon adsorption treatment system was developed and demonstrated under the research project. The results verify the acceptability of this process.

Francis T. Mayo, Director
Municipal Environmental
Research Laboratory

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ABSTRACT

Through the cooperative work of the Environmental Protection Agency, the Aeronautics Commission of Indiana, and Purdue University a research project was conducted to develop a system for the control of pesticide contaminated wastewaters generated by pesticide applicators. This problem was approached in three phases. First, the practices that are currently used to handle pesticide contamination wastewaters were evaluated followed by the development of a system that could be used to collect the pesticide contaminated wastewaters. Finally a treatment plant was developed to remove pesticides from the contaminated wastewaters and produce a high quality effluent.

During the initial phase of the project it was determined that pesticide applicators have between 4 and 20 L of pesticides left in the application equipment when they ave completed a spraying operation. In addition, the wash water used to clean the application equipment has a high concentration of pesticides. The combined wastewater has as much as 20,000 mg/liter total suspended solids and 15,000 mg/liter total Chemical Oxygen Demand. Between 100 and 200 L of wash water are generated with the cleanup of pesticide application equipment.

In the second phase of the research an existing concrete pad, used by an aerial applicator, was modified to control and collect all the runoff from the pad both during the cleaning of the application equipment and following a rain. All wastewater collected on the pad was pumped into a storage tank. This storage tank could then be emptied periodically for treatment with the pilot plant.

A pilot plant was developed to treat the collected wastewater from pesticide applicators. Initially laboratory tests were done to evaluate 3 physical chemical treatment options. First, a flocculation/coagulation/sedimentation step was evaluated using alum as the coagulant. Additional studies were done using filtration and coalescence. A final activated carbon polishing was also evaluated. The results of this work indicated that flocculation/coagulation/sedimentation could be used to remove a high percentage of the pesticides. This step would bring the concentration to the water solubility of the particular pesticide. It was also found that the filtration and coalescence steps were much less effective than the flocculation. The supernatant from the first step was then passed through activated carbon columns. A hydraulic loading rate of .5L/s-m^2 was determined to be adequate with a residence time of approximately 15 minutes. Using this design the capacity of the carbon was approximately 200 mg of pesticide per gram of carbon. The concentration of the pesticides in the clear effluent was usually less than 1 mg/liter.

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This work could not have been completed without the cooperation of numerous pesticide applicators. The personnel of the Southern Crop Service, Inc. in Delray Beach, Florida were especially helpful in supplying initial wastewater samples and in explaning the problems facing pesticide applicators in the Southeastern region of the U.S. ADI Ag Aviation at Monon, Indiana was extremely helpful in allowing us to modify there facilities and collect wastewater samples. Their leadership in ag aviation in Indiana enhanced the project greatly.

The analytical work on this project could not have been completed without the help of Cheryl Towell and Marianne Arbuckle. The assistance we received from the Indiana State Pesticide Office in quality control of pesticide analysis was crucial in evaluating the process.

The completion of this project would have have been possible without the dedicated efforts of Karen Adams and her colleagues of the clerical staff of the Agricultural Engineering Department, Connie Harth, Roxandra Evans and Lisa Houston.

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SECTION 1

1. INTRODUCTION

Pesticide applicators are currently faced with a serious problem created by the management and disposal of the wastewater generated during the cleanup of application equipment. Most treatment systems such as infiltration pits, holding ponds, and evaporation ponds, do not provide adequate safeguards to the environment. Furthermore, no attempt is made to monitor the degradation of specific pesticides. Several elaborate disposal and detoxification processes are currently being evaluated, including incineration and other thermal destruction processes. In order for these more elaborate disposal and detoxification processes to be effectively utilized a concentrated waste would be desirable.

1.1 OBJECTIVES

The purpose of this research project was to develop a field applicable system for containing, concentrating, and removing pesticides from the wastewater that arises during the cleaning and draining of pesticide application equipment. In order to achieve this goal, the following objectives were identified.

1. Evaluation of existing handling, mixing, cleanup and disposal methods in use by commercial agricultural applicators.

2. Development of an acceptable system to prevent spillage during mixing and cleaning of application equipment.

3. Development of an economical wastewater treatment system that could be operated by non-technical personnel and allow for reuse of the treated effluent.

4. Demonstration of the washing and treatment system for wastewater collected from pesticide applicators.

5. Evaluation of the feasibility and economics of such a treatment system.

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SECTION 2

2. CONCLUSIONS

Based on the results of this study it was concluded that the collection and treatment of pesticide contaminated wastewater generated by aerial and ground applicators is feasible.

2.1 COLLECTION OF PESTICIDE WASTE WATER

The following conclusions were drawn about the two techniques used to collect pesticide wastewater.

1. All pesticide waste, rinse, and wash water can be collected in a single storage system. Segregation of the waste into dilute and concentrated portions is not necessary for the proposed treatment system.
2. The wash water from the surface of the aircraft does not contain sufficient quantities of pesticide to warrant inclusion in the collection system, this minimizing the volume of wastewater storage that is required.
3. Most pesticide applicators can adequately rinse out the spray system and wash out the tanks with 100-200 L (25-50 gal) of wash water. The use of high pressure sprayers makes it possible for smaller quantities of water to be used in the cleaning of the equipment.
4. The volume of residue left in the tank of pesticide application equipment may vary from 4-20 L (1-5 gal) depending on the type of application equipment. These residues cannot be pumped out of the tank because of current tank, pump, and piping configurations.
5. Rain water which falls on the collection pad should be diverted away from the storage system. Inclusion of rain water would more than double the amount of wastewater that would need to be stored and treated.

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2.2 TREATMENT OF WASTEWATER

A physical/chemical treatment system was developed and demonstrated. The first step in the system is flocculation, coagulation, and sedimentation. The supernatant produced from this step is passed through activated carbon to remove the remaining pesticide. The following conclusions can be made.

1. The sludge that accumulates during the sedimentation phase of the flocculation, coagulation, and sedimentation process can be suspended and reused for subsequent wastewater treatment, however the solids concentration of the mixture should not exceed 15,000 mg/L.

2. Depending on the type of formulation, the physical treatment process can remove up to 95 per cent of the pesticide material.

3. Activated carbon columns effectively remove the residual pesticides. The capacity of the carbon is approximately 200 mg of pesticide/g of carbon. The hydraulic loading rate on the column should be approximately .6 $L/S\text{-}m^2$ (1 $gal/min\text{-}ft^2$). Residence times of about 15 minutes are required for pesticide adsorption.

4. The pesticide treatment plant developed in this project is capable of removing essentially all pesticide from the wash and rinse water. Residual pesticide concentrations in the water are usually less than 1 mg/L and can be considered safe for reuse as wash water for cleaning the application equipment.

2.3 SYSTEM DESIGN

Based on the research described in this report, the following conclusions can be made:

1. On-site storage of wastewater would require a 3800 L (1000 gal. tank) for bi-weekly treatment or 11000 L (5000 gal) for annual treatment.

2. The low technology system can be operated by a semi-skilled worker with approximately eight hours of training.

3. For aerial applicators a mobile treatment plant that could service all applicators in the state would be the least expensive option. A central plant could be used if all pesticide applicators are included.

4. On-site treatment in a small dedicated treatment plant is possible.

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3. RECOMMENDATIONS

Although the treatment system is well suited for handling pesticide waste generation from a limited scale agricultural spraying operation, further evaluations must be made before widespread application of the system can be expected. The collection and storage of wastewater must be investigated. The cost of the system and means of financing should be considered. Special funds for airport improvement might be used for construction of the washing pad and storage tank. The ground applicator should be able to obtain low cost loans for installation of a system.

One problem that must be studied is the effect of highly mixed pesticide solutions on activated carbon adsorption, particularly for large central treatment facilities where a variety of different pesticide wastes could be expected. One of the most important phenomena to be studied in this regard is the displacement, if any, of some pesticides by other more adsorbable ones. Based on general knowledge of the influent composition, it may be feasible to predict which compound would be discharged first and test for that specific compound. Detailed information on the behavior of carbon with combinations of widely used pesticides will be required before such a method for detecting the exhaustion of the carbon columns could be used.

Another operational aspect, directly related to the above, is the development of a simple, low-cost technique for determining effluent quality. Gas chromatographic investigations may be suitable for laboratory tests, but such technology is not feasible for field application. Bioassay tests and spectrophotometric techniques should be investigated.

No studies have been performed on alternative techniques to dispose of the treatment plant effluent. Irrigation, discharge to streams or publicly owned sewage treatment works are possibilities for the central treatment facility although such means would require careful evaluations of effluent quality and toxicology. Two options which are particularly attractive for on-site treatment both involve water re-use, either as a diluent in the make-up of new pesticide formulations, or as wash water for application equipment. Although our initial studies indicate that the effluent could be used for rinsing purposes, evaluations with a number of other pesticides would have to be carried out before such an alternative could be recommended. Of particular concern in water re-use as a diluent would be herbicide residue. Minor herbicide contamination during an insecticide application could cause crop damage. Hence, water re-use would require meticulous quality control.

Another major problem that must be addressed is disposal of the concentrated residues generated during treatment operations, in particular, the settled alum-pesticide sludge and the spent activated carbon. The most suitable disposal method at this time appears to be containerization of this material and burial in an approved landfill site. However, there are alternate possibilities that are especially applicable to the operation of a large treatment facility. In particular, thermal regeneration of the carbon may be possible. Although it is unlikely that on-site regeneration would be feasible due to the relatively small amount of carbon used. Several manufacturers are now entering into contractual arrangements for carbon pick-up and delivery, with subsequent thermal regeneration. Such an arrangement should be actively pursued. Furthermore, thermal destruction of the contaminated alum sludge may be possible in combination with sewage sludge destruction in multiple hearth furnaces.

Finally, the system must be acceptable to small and large pesticide applicators. Every effort should be made on the part of regulatory officials to aid in the implementation of such a system. As a result of recent federal regulations concerning hazardous waste generation and disposal it is likely that many operators will cooperate in installing such treatment facilities, but they must be made aware of their existence and the ease with which they can be used. In the case of a centrally located treatment facility, the relatively minor effort required for cooperation can be emphasized, while the advantages of compliance with federal regulations and general environmental protection should be stressed.

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SECTION 4

4. BACKGROUND

4.1 TYPES OF PESTICIDES

Pesticides are broadly defined as any chemical compound used to destroy organisms which are considered to be "pests" to man. These chemicals are broken down into a number of subcategories, usually on the basis of target organism such as algicides, defoliants, dessicants, fumigants, fungicides, herbicides, insecticides, lampreycides, larvacides, miticides (acaricides), molluscicides, nematocides, plant growth regulations, repellents, rodenticides, sterilants and synergists. However, this broad chemical spectrum is usually divided into the three dominant pesticide categories, herbicides, insecticides and fungicides.

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4.1.1 Pesticide Usage

According to the USDA (1977) aerial application of pesticides in 1977 accounted for 65 per cent of all pesticides used on agricultural and forest lands, a percentage that has been consistent over the past seven years. The pesticide application industry has sustained an annual growth rate of approximately 12% during the time period between 1971 through 1977. About 8650 agricultural aircraft were in operation at the end of 1977, treating roughly 180 million acres. Helicopters accounted for 12% of the total number of aircraft, with the remaining being fixed wing aircraft of various types. The overall cost of agricultural spraying operations in 1977 was approximately 475 million dollars, of which the following breakdown can be made:

51.3 per cent for weed control
39.3 per cent for insect control
5.4 per cent for pathogen control
1.8 per cent for nematode control

The volume of pesticide usage for the years 1975 through 1977 is shown in Table 1.

It should be noted that U.S. sales of synthetic organic pesticides reached a record high in 1974, which probably contributed to the elevated 1975 usage levels.

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Table 1. Pesticide Usage (USDA, 1977).

	1975 1000's lbs	per cent	1976 1000's lbs	per cent	1977 1000's lbs	per cent
Fungicides	126,829	9.6	132,648	11.1	133,364	10.5
Herbicides	644,575	48.9	557,873	46.8	584,504	46.3
Insecticides	545,916	4.5	502,083	42.1	545,134	43.2

4.1.2 Complexity of Pesticidal Formulation

The term "pesticides" encompasses a large class of compounds covering a broad range of different functions and target organisms. In fact, according to Lawless et al. (1972) there were, as of 1971, over 550 different pesticidal chemicals produced or sold in the United States, and these could be broadly classified in seven major categories and 40 subcategories (Table 2). Furthermore, the problem of disposal of excess solutions of these compounds is further compounded by the number of different formulations in which they are sold. As of 1976 there were approximately 24,000 different pesticide formulations available for interstate shipment and sale, although this number may now be somewhat lower in light of current Federal regulations and restrictions on certain pesticides (Wilkinson, et al. 1978). Furthermore, this does not account for the large number of formulations that are registered solely for in-state sale (approximately 2000 in the state of California alone).

Table 2. Pesticide Classification Scheme (Lande, 1978).

Pesticide Class	Representative Pesticides
1. Phosphorus-Containing Pesticides	
Phosphates and Phosphonates	Moncrotophos, Phosphamidon
Phosphorothioates and Phosphonothioates	Fensulfathion, Ronnel, PennCap-M (microencapsulated methyl) parathion
Phosphorodithioates and Phosphonodithioates	Dimethoate, Disulfoton, Dyfonate, Phorate
Phosphorus-Nitrogen Compounds	Methamidophos
Other Phosphorus-Containing Pesticides	Def
2. Nitrogen-Containing Pesticides	
Carbamates	Carbofuran, Aldicarb, Methomyl
Thiocarbamates	EPTC, Molinate
Dithiocarbamates	Thiram
Amilides	Propanil
Imides and Hydrazides	Captafol
Amides	Diphenamide
Ureas and Uracils	Chloroxuron
Triazenes	Cyanazine, Simazine
Heterocyclic Amines	Amitrole
Quaternary Ammonium Compounds	Paraquat
Aromatic Nitro Compounds	PCNB, Dinoseb
3. Halogen-Containing Pesticides	
DDT Related Compounds	Chlorobenzilate
Chlorophenoxy Compounds	2, 4, 5-T
Aldrin-Toxaphene Group	Endrin
Aliphatic and Alicyclic Chlorinated Compounds	D-D, BHC (Lindane)
Aliphatic Brominated Compounds	DBCP
Dihalogenated Compounds	Dicamba
4. Inorganic and Organometallic Pesticides	Arsenic Acid, MSMA
5. Miscellaneous Pesticides	Sodium fluoroacetate, Creosote, Warfarin

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TYPING GUIDE SHEET

Formulations may differ not only in the physical state of the pesticide (such as emulsifiable concentrates, wettable powders, dusts, or granules), as evidenced by a listing of the most common formulations of carbaryl and malathion in Table 3, but also in the concentration of active pesticide ingredients. Formulations vary, depending on its target organism and manner of application. For example, cotton insecticides are usually applied as emulsifiable concentrates whereas granular formulations are preferred for corn. Furthermore, two or more pesticides, of varying concentration can be included in a single formulation, and currently there are about 500 of these "mixed formulations" available. When the variety of solvents, emulsifiers, and synergists commonly used in these formulations are also taken into consideration, the situation becomes complex.

Table 3. Commonly Used Formulation of Carbaryl and Malathion.

Carboryl - Sevin	
80% S -	— sprayable powder
50% WP -	— wettable powder
5% Bait -	— apple pomace
Sevin 4 Flowable	— aqueous dispersion
Sevimol	— molasses dispersion
Sevin 4-Oil	-- oil dispersion
10% dust	
Malathion - Cythion	
95%	— Malathion ULV concentrate
80.5% EC	— Emulsifiable concentrate
57% EC	— Emulsifiable concentrate
51% EC	— Emulsifiable concentrate
25% WP	— Wettable powder
5% Dust	
4% Dust	

It would indeed be highly impractical, if not impossible, to attempt to develop a waste treatment system that would be applicable for the detoxification/decontamination of all formulations or wastewaters containing the types of pesticides shown in Table 2. Rather, the best approach is to concentrate on the major pesticide classes and/or dominant chemical species. For this purposes of this research, it was decided to concentrate on two of the major pesticide species used in aerial application, carbaryl (Sevin), a widely applied N-alkyl carbamate insecticide of the nitrogen-containing class, and malathion (Cythion) a representative and commonly used phosphorodithioate insecticide of the organophosphate class. The testing of these compounds was justified by the following considerations:

1. Both are widely used in aerial application.

2. Both have relatively low toxicity so as to minimize individual hazard during these introductory stages of plant design and operation.

3. Analytical techniques are relatively simple and thus rapid determination of treatment efficiency is possible.

4. Important subgroups (in terms of possible environmental hazard) of the two major classes of pesticides most commonly used in aerial application would be represented.

Treatment of pesticides in the other five classes could not be stressed because time and people power limitations, and these compounds were not considered to pose as serious a threat to the environment as the nitrogen- and phosphorous-containing compounds. In particular many of the inorganic and organometallic compounds have been banned for use because they contain highly toxic elements (e.g. arsenic, cadmium, and mercury) that cannot be completely detoxified and present significant disposal hazards. The botanical and microbiological pesticides represent only a small fraction of total pesticide usage and are, for the most part, non-toxic to man (although highly toxic to fish). The halogenated compounds represent a wide variety of chemical types, but as a result of their long-term environmental persistence, many have been banned or are under consideration for registration suspension (e.g., 2,4, 5-T). One notable exception is the chlorophenoxy compound 2,4-D, which is still in widespread use. Its persistence is much lower than the highly chlorinated cyclopentadienes and related compounds (aldrin-toxaphene group). Sulfur compounds do not pose a serious environmental or toxicity hazard, and there is no otherwise unclassified pesticide used in sufficient volume in aerial application to justify consideration.

4.2 DISPOSAL OF PESTICIDE WASTE

Pesticide contaminate wastewater, when improperly disposed can lead to a number of undesirable consequences. First and foremost is the danger to public health, most notably in the form of groundwater pollution arising from leaching through contaminated soil, or through direct contamination via surface faults in areas with high water tables. Such contamination is of immediate concern since half of all drinking water is supplied from groundwater and contamination of groundwater poses a threat to public health. Ground surface contamination can pose a threat to children and livestock, while surface runoff can lead to crop damage, poisoning of aquatic life, and contamination of surface water supplies.

4.2.1 Current Regulations Affecting Disposal of Pesticide Residues

The initial legislation for the control of pesticides was the Federal Insecticide, Fungicide, and Rodenticide Act of 1972, which altered and broadened the original 1947 act to address problems of disposal and storage of excess pesticide and pesticide containers, along with regranting the authority for the registration, classification, and cancellation of pesticides. The administrator of the EPA is required under Section 19 of the Act to "establish procedures and regulations for the disposal and storage of excess amounts of such pesticides, and accept at convenient locations for safe disposal a pesticide, the registration of which is cancelled under section b(c), if requested by the owner of the pesticide." Furthermore, "notification of cancellation of any pesticide shall include specific provisions for the unused quantities of such pesticides."

These recommendations, first published on May 1, 1974, provided a general approach to the problem of the disposal of pesticides classified by the EPA as highly or moderately toxic ($LD_{50} < 500$ mg/kg). Exceptions included containers for home or garden use, or those used in farm applications when single containers were to be disposed (usually by open-field burial with due regard to the protection of surface and subsurface water supplies). Recommendations included: (1) recovery of material for further use if large quantities are involved, (2) return to the manufacturer for reprocessing, or, (3) in some cases of cancelled products, export to other countries where use is desired and legal. Export of cancelled products is no longer acceptable. If such alternatives were not viable, incineration of organic pesticides (except those containing mercury, lead, cadmium, and arsenic compounds) was suggested. Burial in an acceptable landfill was suggested if incineration facilities were not available. Soil injection and chemical degradation methods were not urged without the advice of the regional EPA administrator. Similar procedures were suggested for metallo-organic (except organic mercury, lead, cadmium, or arsenic compounds) pesticides. Incineration was considered appropriate after physical and chemical treatment that removed and recovered the heavy metals. Organic mercury, lead, cadmium, arsenic, and all inorganic pesticides were to be treated by chemical deactivation techniques in order to convert the pesticide to non-hazardous products, or if such procedures are not available, encapsulation and landfilling was suggested. Storage in suitable containers was allowed if all other options were not feasible. These recommendations were announced on October 15, 1974, when EPA proposed regulations prohibited the "worst acts" of pesticide disposal.

A far more comprehensive program for the management of pesticides and other hazardous wastes has since been established. This program stems from the authority granted to the administrator of the EPA under the Solid Waste Disposal Act, was amended by the Resource, Conservation, and Recovery Act (RCRA) of 1976 (PL 94-580). In particular, subtitle C of the act creates a "cradle to grave" management control system for hazardous wastes.

Sections under this subtitle relevent to commercial pesticide applicators include: (a) Section 3002, which addresses the mechanics of the manifest system that will track hazardous waste transported from the point of generation to its ultimate disposal, (b) Section 3003, which authorizes standards for transporters of hazardous waste to insure careful handling, (c) Section 3004, which establishes design and operation criteria for hazardous waste treatment, storage, or disposal facilities (TSDF), (d) Section 3005, which discusses the permit granting procedure for facility owners and operators, and (e) Section 3010, which establishes procedures for notifying state or federal regulatory officials of hazardous waste ownership or treatment.

Under the federal regulations (USEPA, 1980) farmers received an exemption if they triple rinse containers (see Table 4) and "dispose of pesticide residues on his own farm in a manner consistent with disposal instructions on the pesticide labels." The exemption does not include commercial agricultural pesticide applicators. Such an individual is considered a hazardous waste generator if the waste generated in one month accumulates to more than "100 kg of any residue," of any chemical listed in the regulation. The list includes numerous pesticides.

Table 4. NACA Triple Rinse and Drain Procedure.

(Shih and Dal Porto, 1976)

1. Empty container into spray tank. Then drain in vertical position in 30 seconds.

2. Add a measured amount of rinse water (or designated spray carrier) so container is 1/4 to 1/5 full. For container size less than 1 gallon, add an amount of rinse solution equal to 1/4 of the container volume. For a 1 gallon container, add 1 quart of rinse solution. For a 5 gallon container, add 1 gallon of rinse solution. For 30 and 55 gallon containers, add 5 gallons of rinse solution.

3. Replace closure. Shake container or roll and tumble to get rinse on all interior surfaces. Drain rinse solution into sprayer or mix tank. Continue draining for 30 seconds after drops start.

4. Repeat the above steps for total of 3 rinses. One gallon and 5 gallon steel containers should be punctured before draining the third rinse. It is recommended that the container be punctured in the top near the front sprout to allow for complete drainage of the third time.

5. For 30 and 55 gallon steel containers, replace closures and secure tightly and send the containers to an approved drum reconditioner (check with State Department of Agriculture for list) or recycle as scrap into a steel melting plant. For 1 gallon and 5 gallon steel containers, crush immediately and recycle for scrap to a steel melting plant. For glass containers, break or crush into large container (such as 55 gallon open headed drum with cover) and recycle for scrap to a glass melting plant. If the above preferred container disposal method cannot be accomplished, the container should be crushed and buried at an approved dump site. Do not reuse containers.

That effect of these extensive regulations on the disposal of commercial spraying pesticide residues is uncertain, especially in regard to the choice between on-site or centrally located off-site facilities, independent of economic considerations. On-site treatment will require compliance standards, established in Sections 3004, 3005 and 3010, while probably easing the responsibilities under Section 3002. Off-site transport is directly affected by Sections 3002 and 3003.

It is not the purpose of this report to address the applicability of the design or operation of the proposed treatment system to current federal regulations. These details can only be clarified over time. Nevertheless, it is almost a certainty that pesticide applicators will, in the near future, have to provide for an acceptable method of detoxification of excess pesticides and contaminated wash waters. The proposed system should be in accordance with the established goals of effective hazardous waste decontamination / detoxification and the minimization of potential environmental insult.

4.2.2 Consideration of Disposal Techniques

A wide variety of destruction, detoxification, or disposal techniques for excess pesticide and contaminated solutions currently exists. These techniques cover a wide spectrum of technical expertise and equipment expense, ranging from highly complex processes, such as microwave plasma destruction to simple alkaline hydrolysis by caustic addition. Despite the wide availability of differing but applicable field disposal technologies, the types of formulations of pesticides that must be treated are so complex that the problem is not finding an applicable disposal technique, but rather finding a technique that will be suitable for a wide range of materials, and within the economic and technical reach of the people who must use it.

In particular, for this research, the development of a treatment system that was suitable for use by aerial applicators, ground applicators and farmers was desired. In designing this system, the following guidelines as adapted from Lawless et al. (1972) were considered.

4.2.2.1 System Requirements

1. The system must minimize the potential for damages to water quality.
2. The system must make minimal contributions to problems of air pollution and solid waste disposal.
3. The system must degrade the pesticide, ideally to a biologically inactive form, or at least convert the material to a less hazardous form.

4.2.2.2 Practical Considerations

1. The layman has only limited equipment and/or financial resources.
2. Treatment chemicals should be readily available and reasonably priced.
3. The layman has limited, if any, experience in treatment chemistry and hazardous waste disposal.
4. Personal hazard should be minimized and the hazards associated with treatment should be no more and preferably less, than those associated with exposure to the pesticide. Generation of dangerous chemical environments (i.e. explosion hazard) must be avoided.
5. The system must be suitable for the variety of different formulation types with which the operator is expected to deal.
6. Treatment must be carried out and completed within a suitably short period of time.
7. The system must be efficient in terms of cost, time, manpower, and pesticide destruction.
8. The system should be, if possible, applicable to existing operation and decontamination procedures and facilities and should not interfere, to any great extent, with application operations. That is, nonproductive time associated with cleanup must be minimized.

4.3 SELECTION OF TREATMENT ALTERNATIVES

Most work dealing with the degradation of pesticides arising from agricultural operations has dealt with loss of toxicity under exposed field conditions. In particular, studies on the rate of microbial breakdown by soil organisms, or soil sorption and subsequent breakdown by bacteria (or various environmental factors) have dominated this area or research (Sandborn et al. 1977). However, the large number of variables present during soil disposal research (such as temperature, pH, soil composition, and moisture) tends to make each research approach unique.

The majority of pesticide disposal research projects have been limited to one of four areas. The first, treatment of industrial wastewaters arising from the manufacture of various pesticides, can give some indication of acceptable alternatives. However, such studies often apply to large volumes of relatively dilute waste streams, that contain a variety of reaction intermediates in combination with generally small amounts of product pesticide. A second major area of research has dealt with the removal of pesticides from drinking water supplies. Most of this work has been concerned with the removal of sub-milligram per liter quantities of chlorinated insecticides. A third course of research has been the development of laboratory-scale facilities for the treatment of "pure" pesticides. However, such data does not accurately describe actual field disposal problems. The fourth research area has dealt with the disposal of "empty" container rinsing and, probably, most closely resembles actual field disposal problems.

The choice of an acceptable disposal method depends on a number of criteria. One of the most fundamental questions to be considered is the total amount of waste that must be disposed. In the case of the aerial applicator, there is not set volume of water which becomes contaminated during tank rinsing and spraying operations (Day, 1976). The volume resulting from equipment washing is difficult to estimate because rinsing procedures and equipment differ with each applicator. Day (1976) estimated that aerial applicators, overall, use 0.4×10^6 m^3/yr. for equipment washing operations. Approximate values can be estimated in light of experience gained in the course of this research. Discussions with Indiana aerial applicators in 1977 yielded suggested that on the average, aircraft are washed about once a day, and occasionally more often when the applicator changes pesticide chemicals. The volume of water and waste generated during cleaning was found to vary from 100 to 2000 L (30 to 600 gal.). However, 190 L/wash (50 gal/wash) appears to be adequate. The amount of excess pesticide left in spray tanks and the method of its disposal was also found to vary, since some operators dispose of the material by spraying on the target field others divert wastewater to a gravel drainage field. The disposal of dilute rinse waters, as opposed to concentrated excess pesticides, will greatly affect the concentration of the overall wash water to be treated and hence the choice of an acceptable treatment method. Other factors which will affect the choice of a treatment procedure will be the permissable pesticide discharge levels, the type of formulation used, and the comparitive costs of equally effective systems.

According to Paulson (1977), the fundamental criterion for determining the manner of hazardous waste disposal is the concentration of the waste stream. Options for disposal of "concentrated waste" include only three alternatives: storage, incineration, and wet air oxidation. A wider variety of options are available for the treatment of "dilute" wastes, including evaporation, reverse osmosis, biological treatment, chemical degradation, ozone (and other oxidants), or adsorption. As can be seen, several of these options do not detoxify the waste but merely concentrate it so that concentrated waste disposal procedures can be used. With the exception of adsorption techniques these options, despite possible applicability to high volume industrial waste treatment facilities, are not feasible for small-scale disposal.

A more detailed list of possible treatment methods for pesticide solutions is given by Lawless, et al. (1972). The specific procedures discussed were concerned with the disposal of small amounts of unwanted pesticides (less than 10 Kg or 200 L (5 lb. or 50 gal.) so that the alternatives evaluated appear to be applicable to this research. A complete listing of conventional disposal alternatives can be derived. These included:

1. Thermal methods -- pyrolysis, incineration, and wet air oxidation

2. Biological methods -- activated sludge, trickling filters, lagoons, anaerobic treatment methods

3. Chemical treatment methods -- pH adjustment acidification, alkalization or neutralization, oxidation (with air, halogens, ozone, etc.),

reduction and photochemical methods (with sunlight or ultraviolet radiation)

4. Physical treatment methods — adsorption (on clays, activated carbon, or synthetic resins), coagulation and flocculation, precipitation, liquid-liquid extraction, and foam infractionation.

Other more recently developed treatment methods include molten salt processes, microwave plasma technology, catalytic ozonation, immobilized enzyme systems, chlorolysis, and metallic couple reduction.

Many of the techniques involve complex and expensive equipment, require highly trained personnel, and cannot be used in a field disposal system, (Wilkinson, et al. 1978). Consequently, not all disposal alternatives were reviewed. Rather, only those processes that were felt to be acceptable for small scale treatment systems were evaluated.

It should be noted that Avant and Bowmer (1979) describe several of the techniques that are currently used to handle wash and rinse water. They concluded that the evaporation pit was the most practical system for the individual applicator. However, this system requires that the evaporation rate in the area be greater than the rainfall or the evaporation pits must be covered. In most regions of the Midwest and Southeast, where large amounts of pesticides are used, rainfall exceeds evaporation.

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4.3.1 Thermal Treatment Alternative

For the disposal of pure pesticides and their formulations, incineration is usually the method of choice. High temperature combustion not only represents the most advanced disposal technology commercially available, but also provides the most effective means of destruction. A description of various types of high temperature incinerators suitable for pesticide disposal was given by Wilkinson et al. (1978).

Wet air oxidation has been found to be capable of hazardous waste detoxification. Reductions in COD from 50 to 95% have been achieved by this method in the treatment of industrial manufacturing wastes. The effluent can be further treated by biological or biophysical polishing (e.g. activated sludge with powdered activated carbon addition) (Wilhelmi 1975).

Studies of thermal destruction of excess pesticides have been conducted by the military. Thermal destruction of 14 chlorinated pesticides under conditions of a 0.4 sec residence time at temperatures of greater than 1000°C (1845°F) and 45-60 percent excess air have proven successful (Shih et al. 1975), and destruction of tonnage quantities of the herbicide "Agent Orange" remaining from the Viet Nam War era, has been carried out by combustion at sea on the M/T Volcanus.

Smaller-scale studies on commonly used agricultural pesticides have been carried out by Kennedy et al. (1969, 1972). In their studies, thermal degradation of 20 pesticides (including carbaryl and malathion) was analyzed. With very few exceptions, temperatures at or near 1000°C were found to be

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sufficient to degrade most commercial pesticide formulations, although it was demonstrated that some materials, such as dicamba, atrazine, paraquat, and bromacil may yield volatile products upon incineration, including such toxic gases as Cl_2, HCl and H_2. Some materials (atrazine, carbaryl, bromacil, and dalapon) left about 10 percent uncombustible residue. The authors cautioned that some toxic residues may remain in the ash.

Wilkinson et al. (1978) claimed that current research indicates that a two sec. residence time at 1000°C should result in 99.99 percent destruction of pesticides. However, such technology is not applicable for field disposal systems because of cost. Hence, incineration is usually limited to manufacturing wastes. Furthermore, problems of feed system clogging and corrosion resulting from high salt formulations may be of concern, along with the spreading of dangerous aerosols containing heavy metals that result from the combustion of organometallic pesticides. Hence, effluent gas scrubbing is essential.

According to Paulson (1977), municipal refuse incinerators cannot be used because:

a. Operating temperatures are not high enough for complete combustion.

b. Residence time in the combustion zone is insufficient.

c. Gas scrubbing is inadequate.

d. High concentration mixtures may not support combustion.

However, a recent study has shown that 99.97 percent or greater destruction of DDT and greater than 99.99 per cent destruction of 2,4,5-T can be achieved in a multiple hearth sludge incinerator when the pesticide is mixed (2 to 5 percent on a dry weight basis) with sewage sludge, (Whitmore, 1975). Such an option may be applicable to the sludges generated by the treatment plant developed in this research.

Putman et al. (1971) have investigated the means for better combustion of pesticides and their containers for the purpose of developing a practical field disposal method. A variety of oxidants were tested for their ability to lower oxidation temperatures, along with various organic binders to prevent the volatilization and sublimation of the pesticides before decomposition. It was found that oxidants were unnecessary in the presence of binding agents and that 99 percent or more of the pesticides tested may be destroyed at the temperatures normally achieved by burning wood, paper, cardboard or plastics. The addition of a mineral oil binding agent to either carbaryl, aldrin, PCB, or DDT significantly aided decomposition at 300°C. Even though mineral oil addition had no effect on diazinon, malathion, or atrazine at 300°C, these pesticides were largely degraded by heat along. Furthermore, only small or negligible amounts of intermediate products of combustion were formed. A variety of potentially toxic combustion gases may be given off, including CO, HCl, Cl_2, and phosgene. Packaging and subsequent melting with heat from polyethylene containers can serve as a suitable substitute for mineral oil.

4.3.2 Biological Treatment Methods

Biological systems including activated sludge, trickling filters, aerated lagoons, and stabilization ponds have been, and continue to be extensively used in the treatment of pesticide manufacturing wastes. However, such systems are subject to rapid upset by a number of different factors, such as "shock" loadings of toxins and rapid pH changes. Furthermore, treatment of pesticide waste often requires nutrient additions and special cultures must frequently be developed for specific types of pesticides.

There are a large number of factors that can affect the biodegradability of a pesticide. Probably the most important of these is the solubility of the compound, since this directly affects its susceptibility to microbial attack. Emulsified forms or highly insoluble material would be expected to be very slowly degraded. The molecular size of the compound can also affect biodegradability, since large bulky molecules may inhibit enzyme approach and hence reduce the rate of breakdown. Furthermore, some chemical structures (e.g., rings) are resistant to biological attack.

Schwartz (1967) illustrated the success of acclimated cultures in the degradation of CIPC in an aqueous system. The maximum concentration of CIPC tested was 5.4 mg/L, and the degradation of the isopropyl side chains was "rapid" with 95 percent degradation in 20 days. A large proportion of the rings and some identified breakdown products of unknown toxicity remained in the system for other two months, although a second culture was capable of complete ring breakage. In the same study, 2,4-D was found to be extremely resistant to biological degradation.

At the present time biological treatment cannot be considered feasible for small-scale systems. First, the quantities of waste are not extensive enough to support an aerobic system, such as activated sludge, while anaerobic systems are especially susceptible to upset by shock loadings. Furthermore, the number of different types of pesticide formulations would indicate the near impossibility of maintaining a suitable acclimated bacterial culture. According to the recommendations of Wilkinson et al. (1978) such methods cannot be endorsed at present because more information is needed on sludge and effluent toxicity (especially in cases of incomplete pesticide degradation) along with the fact that further studies on the volatilization of pesticides in aerobic treatment systems must be done.

However, one biological processes that may in the future be applicable to field disposal systems is the micropit.

Work on micropit disposal was initiated at Iowa State University in early 1977, (Johnson and Baker, 1980) and tests are being conducted to determine the soil biodegradability of atrazine, alachlor, 2,4-D, butoxy ethanol ester, trifluralin, carbaryl, and parathion at relatively low concentrations (0.05 and 0.025 percent). This study was primarily directed toward the development of pesticide disposal methods for farmers and applicators. The study consists of segregating individual pesticide types or classes into separate galvanized metal-lined disposal pits filled with alternate layers of sand and gravel, and monitoring the biological degradation of the pesticide by soil microorganisms.

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The results of this research may help many pesticide applicators since soil microflora have the capability to degrade a wide range of pesticide types.

4.3.3 Chemical Treatment

More research has been carried out in the field of chemical disposal and detoxification of pesticides than for any other disposal means. This situation undoubtedly arises from the fact that chemical disposal combines two major advantages that no other disposal procedure offers. That is, chemical treatment can be easily applied to small batches of pesticide waste, and actual detoxification (rather than segregation and concentration) can often be achieved without resorting to expensive capital equipment, such as incinerators. However, chemical disposal is also prone to some major disadvantages. Specific chemical disposal techniques are usually only applicable to specific types of pesticide wastes. Procedures of more widespread applicability generally require conditions too hazardous for field application. Also, chemical procedures do not always result in complete reaction of all species involved and, furthermore, many possibly toxic functional groups may remain unchanged. As such, the chemical products of a reaction must be characterized and their toxicity evaluated before the proposed reaction can be recommended. Unfortunately data on reaction products is often incomplete or entirely lacking.

At the present time, there does not appear to be any one chemical method that is applicable for the detoxification of all pesticide types, although some techniques appear to be broadly applicable to many pesticide classes.

The chemical methods investigated for possible field use were oxidation, catalyzed reduction, acid or alkaline hydrolysis, and photochemical degradation.

4.3.3.1 Chemical Oxidation

Oxidation can be used to detoxify certain pesticides, although many pesticides have been found to be resistant to a variety of oxidants. In general, chlorinated pesticides have been found to be resistant to chemical oxidation, while carbamates and organophosphates are more amenable. The extent of reaction varies with conditions and concentrations of oxidant dosage.

Faust and Aly (1964) found various forms of 2,4-D to be highly resistant to the oxidizing effects of chlorine gas (Cl_2) or potassium permanganate ($KMNO_4$) although $KMNO_4$ was found to be quite successful in the oxidation of 2,4-dichlophenol (1.25 ppm of $KMnO_4$ per 1 ppm of 2,4-DCP caused 100 percent oxidation in 15 min. at pH 7). Cohen, et al. (1960) found that rotenone could be reduced from 0.1 to 0.005 ppm by chlorination. However, high chlorine dosages were required (38.5, 29.5, and 11 mg/L of chlorine were required to complete the oxidation in 15, 60, and 180 minutes, respectively). Chlorine dioxide was found to be much more effective oxidant but, as would be expected, toxaphene was found to be inert to oxidation by chlorine.

According to Robeck, et al. (1965), neither 8 nor 50 mg/L of chlorine caused any detectable oxidation of dieldrin or lindane. Parathion was 97 percent removed at 7 ppm but the more toxic intermediate, paraoxon, was produced as a result of this oxidation. Studies with potassium permanganate showed that dosages as high as 40 ppm produced less than a 10 percent reduction of 10 ppb levels of dieldrin, lindane, 2,4-D and 2,4,5-T. A 17 percent reduction in parathion concentration was observed. Studies were also performed using ozone. Table 5 shows that only limited removal of the chlorinated compounds occurred at high and impractical concentrations of oxidant, although parathion was much more responsive to oxidation. Chlorinated pesticide breakdown products were not characterized.

Table 5. Pesticide Oxidation by Ozone.

Compound	Ozone dose	Percent decrease
Lindane	38	35
Diedrin	36	50
DDT	36	94
Parathion	10	94

Beuscher, et al. (1964) studied three chlorinated pesticides, with concentrations of 1 to 10 mg/L for Lindane and 0.1 mg/L of aLdrin and dieLdrin. It was found that lindane was oxidizable by ozone, partially oxidizable by $KMnO^4$ and unaffected by chlorine and peroxides. Oxidation of dieldrin was limited to ozone. Aldrin was attacked by everything but peroxides. This study suggested that volatility might be used as an indication of oxidizability, since aldrin was the most volatile of the species tested.

Leigh (1969) tested the removal of lindane, heptachlor, DDT, and entrin with chlorine, hypochlorite, potassium permanganate and potassium persulfate. Hypochlorite and permanaganate were found to have no effect on lindane and endrin. Hypochlorite was more effective on DDT than was permanganate, but permanganate was much more effective in the oxidation of heptachlor.

Currently there are three pesticide detoxification methods using ozone gas and some form of catalysis. These methods include combinations of ozone and ultraviolet light, chemical catalysis of ozone, and ozone with sonocatalysis (Wilkinson et al. 1978). At present, only the first method, ozone/UV is used on a large scale, and promising results have been obtained. Mauk et al. (1970) have reduced initial concentration of 50 mg/L of PCP, malathion, metham, and baygon to <0.5 ppm and have reduced 58 ppb of DDT to <0.5 ppb in 90 minutes. It has been claimed that the system is only 10 percent more expensive than activated carbon treatment (when replacement costs are considered) although capital cost is at least twice as high (Prengle and Mauk, 1976).

Ed-Dib and Aly (1977a) investigated the oxidation efficiency of chlorine, with and without UV light catalysis, and chlorine dioxide. Solutions of 8 to 10 mg/L of the pesticide were treated with approximately equal concentrations of oxidants. Phenylcarbamates (IPC and CIPC) were generally unaffected by chlorination, showing a maximum removal of only 10 percent. Greater efficiency, ranging from 23 to 70 percent destruction was attained with various anilide and phenylurea pesticides. As in other studies, chlorine dioxide was found to be a more effective oxidant, with the phenyl carbamates showing 30 percent degradation while 40 to 80 percent was seen with anilides and phenylureas. However, the amide linkage, which is responsible for a number of undesirable effects, was largely unaffected and, therefore, post oxidation aniline derivatives may impart some of the same toxic effects as the parent pesticides.

4.3.3.2 Chemical Reduction

Kenedy et al. (1972) applied a sodium biphenyl reducing agent to 20 major pesticides to test the degree of degradation. Analytical interferences limited product determination to only five species. It was found that trifluralin and paraquat showed greater than 90% and 95% degradation respectively. However, it was noted the biphenyl reagent is unstable above $0^{o}C$ and hence its use is not recommended because of safety considerations. Metallic sodium or lithium in liquid ammonia was also tested with great success. Sixteen pesticides showed complete degradation, while carbaryl and paraquat showed greater than 90 percent destruction. However, these reagents create a hazardous reaction environment and are not recommended for field use.

A method of reductive degradation of a variety of chlorinated compounds has been recently developed (Anon, 1976). Amenable compounds include cyclodiene pesticides (aldrin, endrin, etc.), DDT and related materials, chlorinated camphenes (toxaphene), lindane, and chlorinated phenoxy acetic acid derivatives. The process uses a catalyzed iron reducing agent in a sand bed matrix. Costs of treatment, based on a 100-gpm (378L/m) unit, are in the vicinity of 72 cents per 1000 gal. (19 cents/1000 L) treated.

4.3.3.3 Acid or Alkaline Hydrolysis

Hsieh et al. (1972) discussed alkaline hydrolysis kinetics and efficiency for treatment of rinsing arising from various emptied containers of parathion, and showed that degradation did not follow the expected first order (with respect to hydroxide) kinetics. This unexpected kinetic pattern may have resulted from the presence of emulsifiers as well as the low water solubility of parathion, that interfered with nucleophilic attack. Addition of methanol to increase pesticide solubility greatly increased the degradation rate. Wolfe et al. (1977) gave a detailed description of pathways and products for acid and alkaline hydrolysis of malathion and showed that acid hydrolysis results in a slow degradation rate. Cowart et al. (1971) discussed the degradation by hydrolysis of dilute (<2 mg/L) solutions of seven organophosphate pesticides in natural aqueous systems and found that the hydrolysis rate increases with decreasing sulfur content. El-Dib and Aly (1976) found that phenyl carbamates were readily susceptible to alkaline hydrolysis, while anilides were less reactive and phenyl ureas were the least reactive. All the pesticides tested were stable for at least 4 months in the pH range of 6 to 9. The rate of hydrolysis increased 2 to 3 times for each $10^{o}C$ rise in temperature.

Although the susceptibility of the organophosphate pesticides and some members of the nitrogen-containing class to alkaline hydrolysis has been well documented, such a technique cannot be indiscriminately applied to all members of these classes. Based on production volume, toxicity, soil persistence, mobility, and chemical structure, Shih and Dal Porto (1976) chose twenty key pesticides from the major classes of the nitrogen-containing, phosphorus-containing, and halogenated insecticides for evaluation of chemical disposal techniques. Alkaline hydrolytic degradation was recommended for only seven of the twenty compounds: naled, diazinon, guthion, malathion, carbaryl, captan, and atrazine. No practical disposal method was found for the remaining pesticides — dursban, methyl parathion, maneb, alachlor, diuron, picloram, trifluralin, methoxychlor, chlordane, toxaphene, 2,4-D, amiben, and pentachlorophenol. Pesticides were determined to be unsuitable for chemical detoxification if; 1) the extent of reaction was incomplete of unknown, 2) expensive or hazardous chemicals were required, and/or 3) hazardous end products were generated. Although all the compounds that were hydrolyzable were either organophosphates, carbamates, imides, hydrazides, or triazines, not all members of these classes could be hydralyzed. The authors stated that because the hazard of the end product is dependent on specific functional groups, each chemical must be judged on an individual basis. However, the unsuitability of alkaline hydrolysis for one member of a class can often given warning for other members as well. For example, diuron yields a more toxic 3,4-dichloroaniline product, while closely related monuron produces an aniline product. Stewart et al. (1967) and Bender (1969) discussed the toxicity of hydrolysis products of carbaryl and malathion.

Alkaline hydrolysis is not recommended for the halogenated pesticides because of the difficulty in replacing halogen atoms, and the fact that the degradation products are almost always unknown (Shih and Dal Porto, 1976). These considerations apply to other forms of chemical treatment as well, where reagents are often compound-specific, hazardous, and expensive.

Shih and Dal Porto (1976) found a variety of pesticides to be unsuitable for acid hydrolysis. Slow reaction rates were seen for atrazine, malathion, and methyl parathion, (which also gives rise to toxic P-nitrophenol). Compounds resulting in toxic products or products of unknown toxicity include maneb, alachlor, diuron, trifluralin, and ambien. Captan is unaffected by acid treatment.

Hydrolysis can sometimes be used as a treatment after chemical oxidation for the removal of toxic intermediates. Goman and Faust (1972) have shown this to be true for parathion degradation.

The work of Shih and Dal Porto (1976) was continued by Lande (1978) who chose forty pesticides. Only eleven pesticides were recommended for disposal by alkaline hydrolysis, including three carbamates, seven organophosphates and one imide. Rejected compounds included four organophosphates, two thiocarbamates and two triazines.

Kennedy et al. (1969) tested alkaline hydrolysis on a number of pesticides using NaOH and NH_4OH. Neither method was found to give complete eraction of the compounds tested.

4.3.3.4 Photolysis

A variety of pesticides have been shown to exhibit a number of chemical changes upon exposure to ultraviolet radiation or natural sunlight (Abdel-Wahab and Casida 1976, Weldon and Timmons 1961, Jordan et al. 1964, Crosby et al. 1965, Eberle and Gunter 1965) although these changes may result in more toxic forms of the parent pesticides. For example, more toxic photodieldrin and photoaldrin may be formed when dieldrin and aldrin are exposed to sunlight (Robinson et al., 1966, Rosen and Sutherland, 1967, and Plimmer, 1978).

In order to undergo photo decomposition, light energy must first be absorbed. Since most of the ultraviolet radiation emitted by the sun is absorbed in the ozone layer, only pesticides adsorbing above 285 nm can be expected to undergo natural photolysis. Such considerations are, of course, not meaningful when an artificial ultraviolet light source is utilized.

Absorbed light energy may cause a variety of reactions within the pesticide molecules. Frequently, free radicals that may cause isomerization, substitution, or oxidation may arise. The reaction is heavily dependent on the chemical environment in which it takes place. One advantage to photochemical breakdown is that it also may lead to enhanced susceptibility to biodegradation.

Many compounds require a photo-sensitizing agent or a hydrogen donor that serves to capture light energy and transfer it to the pesticide. Examples of this include acetone for the cyclodiene pesticides (Plimmer 1978) or the use of olive oil for TCDP decontamination (Crosby 1978).

Aly and El-Dib (1971) studied photochemical breakdown of three carbamate pesticides, carbaryl, baygon, and pyrolan. The effects of pH were found to vary. The primary result of irradiation appeared to be cleavage of the ester linkage although Crosby et al. (1965) reported that photodecomposition of carbaryl yielded, in addition to 1-naphthol, several other compounds having an acetyl cholinesterase inhibition potential, thus indicating carbamate ester group integrity.

Mitchell (1966) tested the effect of ultraviolet light on 141 different pesticides. Thirty were found to undergo little or no degradation, while complete or practically complete degradation was seen for 32 pesticides with a 60 minute exposure time. Based on these findings, the procedure appears to be well suited for the partial or complete breakdown of organophosphorous pesticides, but the identity and toxicity of the products were not determined.

It must be remembered that most of these studies have been performed in the laboratory and/or in actual soil application procedures where small amounts and thin layers of material have been involved. The necessity for providing adequate light penetration and contact time for the larger batches of concentrated materials expected from field operations severely limits the practicality of photochemical degradation treatment processes.

At this time, there is no chemical disposal of detoxification technique that can be pursued for application in a field disposal system. Although, many such techniques can be effective, most of these are limited to relatively few pesticides and hence have no broad range of applicability. Many of these techniques are only partially effective and give rise to hazardous products, the toxicity of which has yet to be determined. Since many of the proposed techniques require hazardous chemicals and reaction conditions with which the layman is often inexperienced, chemical disposal practices for field pesticide decontamination cannot be recommended at this time.

4.3.4 Physical Treatment Methods

A variety of physical treatment methods can be applied to the control of pesticide wastes. Most of the research in this area has been concerned with the removal of pesticides from relatively "clean" water. Because it is often more difficult to achieve significant percentage removals of compounds from dilute solutions than from concentrated waste streams, it would appear that the technology used for water treatment would be equally or more effective for the treatment of pesticide contaminated wastewater for aerial applicators.

Physical treatment methods do not result in destruction or detoxification of the hazardous materials, but rather in the removal and subsequent concentration of materials through phase separation procedures. Therefore, other means are required to achieve ultimate decontamination of the waste. The physical treatment methods most commonly used are coagulation/flocculation and adsorption (on resins or activated carbon). Only one study dealing with the treatment of several chlorinated pesticides by foam fractionation was found to be applicable to pesticide cleanup applications (Whitehouse 1971) and, hence, that technology was not considered.

4.3.4.1 Resin Adsorption

Depending upon the individual chemical considered, pesticides can be removed on one of three types of synthetic resins used in water and wastewater treatment, that is anionic and cationic exchange resins as well as more recently developed hydrophobic resins. Because the number of pesticides that will respond to cationic resins (for example, positively charged, highly soluble compounds such as paraquat and diquat) or anionic resins (such as the ionized acidic pesticides of the chlorophenoxy acid class) are very limited when compared to the total number of commonly used non-ionic or weakly charged pesticides, ion-exchange resins were not considered to be a viable treatment alternative for all classes of pesticides. For the same reason, the use of clays with high cation exchange capacity (CEC), such as montmorillonite or kaolinite, were not considered to be acceptable treatment alternatives except when specific pesticides such as diquat or paraquat are in the wastewater. However, hydrophobic resins, such as Amberlite XAD-2 and the more recently developed, higher capacity XAD-4 resin, appear to have potential application for the treatment of most pesticides.

Kennedy (1973) examined the removal of chlorinated pesticides on hydrophobic resins in laboratory scale columns (1.77 cm i.d.). At a flow rate of 0.125 gpm/ft^2 and an influent pesticide concentration of 33.5 mg/L, no pesticide breakthrough was reported after 120 bed volumes had passed through the column. Breakthrough was seen almost immediately in a similarly operated activated carbon column. The carbon effluent contained about 1 mg/L of pesticide after 70 bed volumes and was essentially exhausted after 110 bed volumes. Performance of the resin after regeneration of both beds with isopropanol and methanol was also found to be superior to the carbon, with the resin showing a capacity of approximately 1.5 times that of the carbon bed with significantly less leakage of pesticide in the early stages of operation. It should be noted that the great majority of pesticides were recovered from the resin with two bed volumes of isopropanol regenerant. Acetone gave superior regeneration performance but was dismissed because of its flammability.

Leenheer (1970) found excellent removals of carbaryl and parathion on XAD-2 resin. A large scale industrial application of hydrophobic resin adsorption of pesticide manufacturing wastes is currently being conducted at Velsicol Chemical Company in Memphis, TN (Wilkinson et al. 1978).

Although resin adsorption appears to hold great promise for the treatment of pesticide-bearing wastewaters, the hazards associated with the use of solvents and the recovery of volatile regenerant chemicals make the system uneconomical and impractical for small-scale applications at this time. Furthermore, the problems of disposal of concentrated pesticides remaining solvent recovery still remain.

4.3.4.2 Reverse Osmosis

The process of reverse osmosis (R.O.) has been used to treat many different pesticides. Edwards and Schubert (1974) evaluated three different membranes for the treatment of water supplies containing 2,4-D waste. For cellulose acetate, cellulose triacetate, and polyelectrolytic membranes, maximum retention of the sodium salt formulation of 2,4-D never exceeded 65 percent and in most cases ranged from 1 to 51 percent although it was noted that treatment of the ester compounds was more successful.

Chian et al. (1975) tested the removal of 13 major pesticides on two R.O. membrane types, conventional cellulose acetate and a cross-linked polyethylene imine with m-tolulene 2,4 diisocyanate. Excellent separation was obtained, although values were only in the 1 mg/L or less concentration range (Table 6). In many cases, removal was largely due to pesticide adsorption on the membrane. Hinden et al. (1969) also obtained high percentage removals for several chlorinated pesticides (84 percent for lindane, >99.5 percent for DDT and DDD and 52 percent for BHC), but only dilute solutions (<mg/L) were tested.

Reverse osmosis cannot be recommended for field disposal units at the present time for a number of reasons. The system is relatively expensive and, to date, untested on a large number of pesticides. The effect of mixed solutes must be further investigated, since a variety of effects such as concentration polarization, gel formation, dynamic membrane formation, complex formation, and "salting out" may occur (Edwards and Schubert (1974)). Also, since a great deal of pesticide removal occurs by adsorption onto the membrane, the behavior of the system after exhaustion of the sorptive capacity of the membrane has been reached must be investigated. To date, no such long-term studies have been carried out. Finally, most work with reverse osmosis has dealt with very dilute pesticide solutions. The effect and efficiency of removal of high concentration waste remains unexamined.

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Table 6. Removal of Chorinated Pesticides by Reverse Osmosis

Amount of Pesticides (mg/L) in solutions

Pesticide	Membrane	Origional feed	Reten-tate	Permeate	Adsorbed calcd[a]	% removal	% adsorp-tion calcd[b]
Aldrin	NS-100	142.3	6.9	N.D.[c]	135.4	100	95.15
	CA		29.1	N.D.	113.2	100	79.55
Lindane	NS-100	506.4	440.2	5.3	60.9	98.95	12.03
	CA	157.5	2.5	346.4	99.51	68.40	
Heptachlor	NS-100	145.1	5.4	N.D.	139.7	100	96.28
	CA		28.1	N.D.	117.0	100	80.63
Heptachlor epoxide	NS-100	306.9	25.6	0.5	280.8	99.84	91.50
	CA		71.5	0.7	234.7	99.77	76.47
DDE	NS-100	69.0	4.2	N.D.	64.9	100	94.06
	CA		13.6	N.D.	55.4	100	80.29
DDT	NS-100	42.0	2.4	N.D.	39.6	100	94.29
	CA		N.D.	N.D.	42.0	100	100
Dieldrin	NS-100	321.3	14.9	N.D.	306.4	100	95.36
	CA		75.7	0.4	245.2	99.88	76.31
Diazinon	NS-100	473.7	273.5	56.6	143.6	98.05	30.31
	CA		334.7	8.3	130.7	98.25	27.59
	NS-100	913.1	542.1	4.0	370.6	99.56	40.59
	CA		496.9	4.1	412.1	99.55	45.13
	NS-100	1057.8	647.0	3.7	407.1	99.65	38.49
	CA		739.9	8.9	309.1	99.16	29.22
	NS-100	747.3	363.2	1.3	382.8	99.83	51.22
	CA		412.5	0.9	333.9	99.88	44.68
Randox	NS-100	326.8	286.0	4.7	36.1	98.56	11.05
	CA		253.7	91.4	18.3	72.03	5.60
Trifluralin	NS-100	1578.9	530.0	0.1	1048.8	99.99	66.43
	CA		560.0	4.1	1014.7	99.74	64.27
Atrazine	NS-100	1101.7	956.5	24.0	121.2	97.82	11.00
	CA		851.4	176.0	74.3	84.02	6.74
Captan	NS-100	688.9	437.0	N.D.[b]	252.4	100	36.64
	CA		314.7	8.4	440.1	97.78	63.88

[a] Adsorbed calcd = pesticides present in the original feed less that determined in the retentate and permeate.
[b] (Pesticides adsorbed calcd)/(pesticides in original feed) x 100%.
[c] N.D. = nondetectable.

4.3.4.3 Coagulation/Flocculation

There are different interpretations in the technical literature of the terms "coagulation" and "flocculation" especially in regard to wastewater treatment. For the purpose of this discussion, coagulation will refer to the overall process of particle aggregation to achieve larger, more settleable masses or "flocs" while flocculation will be used to describe the transport of these materials by gentle stirring or agitation in order to accomplish particle aggregation.

Perhaps the earliest study of pesticide removal from water was carried out by Carollo (1945) in response to post-war concern about DDT contamination. Ferric chloride and alum (aluminum sulfate) were used as coagulants for DDT-contaminated water. Treatment consisted of coagulant addition, flocculation for 30 minutes and subsequent filtration or sedimentation. Only low dosages (7.4 to 8.5 ppm) of coagulant were applied. Results are summarized in Table 7.

It should be noted that the pesticide contaminant was suspended in solution and that treatment probably did not remove any dissolved material.

Table 7. Effect of Coagulation/Flocculation on DDT Removal (Carrolo, 1945)

Coagulant	Coagulant Dose mg/L	DDT Conc. (initial) mg/L		% Removal DDT
alum	7.4	.1	settled 1 hr	40%
alum	7.4	1-10	settled 1 hr	50%
alum	8.5	.1	filtered	84%
alum	8.5	1-10	filtered	95%
ferric chloride	7.4	.1	settled 1 hr	60%
ferric chloride	7.4	1-10	settled 1 hr	80%
ferric chloride	8.5	.1	filtered	80%
ferric chloride	8.5	1-10	filtered	91%

Robeck et al. (1965) demonstrated the effectiveness of coagulation and filtration for the removal of a number of pesticides from water. Solutions of DDT, parathion, dieldrin, 2,4,5-T ester and endrin were prepared by forming emulsions of these materials in concentrations ranging from 1 to 25 ppb. With the use of these conventional water treatment practices, removal from dilute solutions could be expected to be 80 percent for parathion, 55 percent for dieldrin, 65 percent for 2,4,5-T esters, 25 percent for endrin, and 100 percent of DDT. Lime-soda softening with an iron salt coagulant did not produce significantly different results than were observed with alum coagulation, except that somewhat poorer removals were seen for DDT and dieldrin. The variety in the measured degree of removal was probably accounted for by differences in solubility and affinity for surfaces.

Whitehouse (1971) used nine different coagulation/flocculation methods, including combinations of alum, five different polyelectrolytes, ferric sulfate, clay and activated carbon for the removal of malathion. Pure solutions, not formulations, were used for these studies, therefore, the solubility of the material was probably much greater than would be expected in a powder or emulsifiable concentrate-based solution. Results were not encouraging for the removal of malathion. Coagulants alone accomplished less than 10 percent removal while the introduction of polyelectrolytes showed little effect. Solution concentrations ranges from 100 to 180 mg/L (note the water solubility of malathion is 145 mg/L). Alum coagulation failed to remove dilute concentrations of toxaphene (0.14 mg/L) and rotenone (0.17 mg/L) with applied coagulant dosages as high as 100 mg/L.

Schwartz (1962) studied the removal of 2,4-D in natural waters. Alum and ferric sulfate achieved about the same degree of removal as that resulting from the settling of the natural silt in water, that is 3 to 6 percent. Dosages of the pesticide ranged between 3-15 mg/L.

El-Dib and Aly (1977a) tested alum and ferric sulfate coagulation on a variety of pesticides. Solutions were prepared from pure (non-formulated) pesticides to a concentration of 8 to 10 mg/L. Alum dosages of 20 mg/L were completely ineffective while dosages of 100 mg/L accomplished only 10 percent or less removal of pesticide. Ferric sulfate was slightly more effective, and the results can be summarized in Table 8. Note that greater coagulant dosages gave consistently greater removals.

Table 8. Feric Sulfate as a Coagulent for Pesticide Removal
(El-Dib and Aly, 1977)

Pesticide	% Removal of Pesticide	
	50 mg/L	100 mg/L
IPC	0	5
CIPC	10	21
Monvron	5	15
Diuron	8	20
Linvron	10	30
Nebvran	11	22
Stam	0	8.6
Karsil	10	20
Dicryl	0	5
Vitavax	10	20

Initial inspection of the literature would appear to show that coagulation is an ineffective means of accomplishing pesticide removal. However, two factors must be kept in mind in the interpretation of these results. First, most studies have been performed on dilute pesticide solutions. Secondly, the majority of studies have dealt with solutions prepared from pure pesticides. As such, the results do not necessarily model those that might be expected from treatment of aerial application waste where formulated pesticides will be treated and relatively high pesticide concentrations are expected.

Consequently, it was decided to investigate coagulation and flocculation as a treatment alternative as well as to evaluate filtration and oil coalescence. The latter processes are not substantially different from coagulation but merely differ in the manner used to achieve physical separation.

4.3.4.4 Activited Carbon Adsorption

Numerous studies during the past fifteen years have shown activated carbon to be an effective means for the removal of pesticides from water. Whitehouse (1971) found activated carbon to be the most effective treatment method for malathion, 2,4-D, DDT, aldrin, and dieldrin. Activated carbon use in a field treatment system for pesticide disposal is attractive from a number of standpoints. This material has long been known as an effective adsorbent for ring compounds and other slightly soluble materials (a characteristic shared by many pesticides) and the high adsorption capacities exhibited by carbon, along with the relatively low purchase price ($1.50/kg) makes its use economically attractive. Furthermore, the efficiency of the adsorbent in the removal of low concentrations of material indicates the possibility of producing a high quality effluent. Even though the performance of activated carbon may vary under differing conditions of temperature and pH, such conditions are not expected to undergo a great deal of variation in actual field situations. However, one factor that may have significant effect on performance is the highly mixed nature of adsorbates arising from the mixing of a variety of wash solutions, many of which may be in sufficient quantity to cause competition and displacement on the carbon.

A detailed study of the mechanics of activated carbon adsorption of a variety of pesticide types was carried out by Weber and Gould (1966). The pesticides studied included a number of dinitrophenols and chlorophenoxy acids along with carbaryl and the highly toxic phosphorothioate, parathion. Adsorption parameters were determined by a batch shaking technique using a commercially available activated carbon of specified size.

Within the classes of compounds studied, the rate of removal was found to be fairly consistent, that is, the rate of pesticide removal was relatively independent of the type of compound. Changes in adsorption rate caused by concentration changes were also found to be consistant, in that increased concentrations of pesticides led to increases in the adsorption rate in a predictable manner. The data were found to fit a Langmuir isotherm and comparison of "b" values, a measure of the energy adsorption, showed similarity for all the compounds tested with the exception of parathion, whose high value indicated exhaustion capacity could be achieved at low pesticide concentrations. The authors stated that removal of low concentrations of pesticides would likely be more efficient than that indicated by the isotherm graph. These findings indicate the broad applicability of carbon adsorption to pesticides of various classes. Exhaustion capacities of the carbon were found to range from 387 mg/g (38.7 percent) for 2,4-D to 530 mg/g (53 percent) for parathion.

Hyndshaw (1962) conducted studies on carbon adsorption of a number of chlorinated hydrocarbons, chlorophenoxy acids and organophosphates. Dosages of 29 mg/L or less of activated carbon produced a 90 percent or greater reduction for solutions containing as much as 50 mg/L of pesticide.

Schwartz (1967) tested the effectiveness of removing CIPC with activated carbon. At a pH of 6.9 and 20°C, 5 mg/L of CIPC was reduced by 90 percent within 2 hours and 98 percent removal was observed within 22 hours with 100 mg/L additions of powdered activated carbon (PAC). Under similar conditions 25 and 50 mg/L PAC removed 56 percent and 95 percent of CIPC, respectively, at initial concentrations of 10 mg/L. Approximately 90 percent of the adsorption occurred within the first four hours. Adsorption data were found to follow a Freundlich isotherm, although a Langmuir isotherm was found to be equally applicable in the higher concentration ranges. The ultimate capacity of the carbon ranged from 29.1 to 33.4 percent by weight. Adsorption was independent of pH in the range of 4.8 to 9.3. Other work by Schwartz (1962) showed PAC to be effective in the removal of 2,4-D. A concentration of 10 mg/L was reduced 60 percent by the addition of 100 mg/L PAC and greater than 99 percent removal of 0.1 mg/L was achieved with carbon at 50 mg/L. Optimum pH was found to be 3.

Ward and Getzen (1970) studied adsorption of three related herbicides: 2,4-D, dicamba, and ambien, in order to determine the influence of pH. Their results correlated well with those of Schwartz (1962) in showing that a reduction in solution pH from 7 to 3 increased the extent of adsorption, indicating that sorption of the molecular species is favored over the ionic form. Sharp increases in adsorption were noted in the pH range of 6 to 4, apparently because of increased hydrogen ion adsorption onto the carbon, which enhanced the removal of negatively charged acidic herbicides. Ward and Getzel (1970) also observed that increased chlorination of the ring structures led to increased adsorption on the carbon. These results are in agreement with those of Leopold et al. (1960), who showed substitution of chlorine atoms on phenoxy acetic acid rings lowered water solubility and increased adsorption. When the relative adsorptions of the herbicides were compared, it was found that the least soluble herbicides, monuron, CIPC, and IPC were the most high adsorbed (Table 9). Note that the acidic nature of the poorly adsorbed compound.

Table 9. Absorption of herbicides on activated column.

Herbicide	Chemical Name	% Adsorption
Monuron	3-(p- chlorophenyl) 1,1 diethyl urea	98
CIPC	isopropyl N(3-chlorophenyl) carbamate	98
IPC	isopropyl N-phenyl carbamat	96
Naptalam (NPA)	N-1-naphthyl phthalamic acid	82
2,4,5-T	2,4,5 Trihloro acetic acid	65
2,4-D	2,4 dichloro phenoxy acetic acid	49
TBA	Trichloro benzoic acid	32
TCA	Trichloro acetic acid	13

However, Leopold et al. (1960) disagrees with the results of previous studies in stating that no effect was seen in the adsorption of 2,4-D in the pH range of 2.2 to 8. Aly and Faust (1965) also performed laboratory studies on removal of 2,4-D and its derivatives by conventional water treatment techniques, including activated carbon, which was found to be the most effective method for removing 2,4-D, 2,4-DCP, and the odor-producing substances in the formulations. The 2,4-D adsorption data were found to follow a Freuendlich isotherm and in keeping with previously discussed studies, an inverse relationship between adsorbability and solubility was noted. The ester forms of the pesticide required significantly less carbon dosages than the corresponding ionizable salt.

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Activated carbon has been evaluated with a variety of other chlorinated compounds. Bernardin and Froelich (1975) performed a number of studies with powdered FS-300 (Filtrasorb) carbon. Data were found to fit a Freundlich isotherm and are summarized in Table 10. Note that the low capacities are a direct result of the low pesticide concentrations applied and do not reflect exhaustion capacity. Among other studies Greve and Witt (1971) have shown endosulfan to be amenable to activated carbon treatment.

Table 10. Activated carbon adsorption of chlorinated pesticides.

Pesticide	Initial conc. (mg/L)	Final conc. (mg/L)	Capacity (by weight) carbon at initial conc.
Aldrin	19	1.0	3.0
Dieldrin	62	.08	1.5
Endrin	41	.07	10.0
DDT	41	.15	1.1
DDD	56	.14	13.0
DDE	38	1.0	.9
Toxaphene	155	1.0	4.2

Although Carollo (1945) showed DDT removals by flocculation, significantly better removals were observed when activated carbon was included in the treatment process. Concentrations of 1 mg/L of DDT were completely removed with the addition of 7.4 mg/L alum, filtration and mixing with 1.65 mg/L of activated carbon. Cohen, et al. (1960) found carbon to be successful in the removal of the fish poisons rotenone and toxaphene. The data were found to fit a Freundlich isotherm, from which the following information could be predicted; 9 mg/L of activated carbon could reduce 0.14 mg/L toxaphene to .014 mg/L, 6 mg/L could reduce this concentration to 0.058 mg/L and an effluent concentration of 0.085 would be expected with a carbon dose of 3 mg/L.

Whitehouse (1971) worked with activated carbon for the treatment of a variety of pesticides. Solutions of 50 mg/L of 2,4-D required 1 gram of carbon to achieve complete removal in 1 hour whereas 100 percent removal of dieldrin and DDT was obtained with carbon dosages of 100 mg/L in 3 hours. In keeping with previous findings, 2,4-D adsorption was enhanced by dropping the pH. Of particular interest are detailed studies by Whitehouse (1971) on carbon adsorption of malathion. In batch shaking tests of two hour duration, 100 percent removal of 5 to 10 mg/L malathion was accomplished with carbon dosages of 80 mg/L, while the complete removal from a 25 mg/L malathion solution was accomplished with 140 mg/L of carbon. Such high capacities shown for batch equilibrium studies seem to promise highly successful operation of a carbon column.

Prometone, 2,4-D, paraquat, and diquat adsorption were all found to follow a Freundlich isotherm (Weber et al., 1968). The inverse relationship between solubility and adsorbability appeared to hold since prometone was the most strongly adsorbed of the four compounds. Paraquat was found to be more strongly adsorbed than diquat, results that correlate with those of Faust and Zarins (1969). Here, as well, results could be described by a Freundlich

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isotherm. Paraquat and diquat removal by activated carbon addition was found to be feasible with a contact time of 30 to 60 minutes, but the required carbon dosages were high when compared to other pesticides. This is not surprising since paraquat and diquat exist in water as ionic, soluble species. In particular, reduction of 10 mg/L of diquat down to 0.1 mg/L required 900 mg/L of carbon, while similar reductions in paraquat required 450 mg/L at a 30-minute contact time. A reaction time of 60 minutes reduced the required carbon dosage to 629 mg/L and 456 mg/L respectively. No attempt was made to evaluate carbon column operation.

Coffey (1969) used a root growth bioassay technique to evaluate adsorption efficiency. Contrary to the results of previous investigators, he found activated carbon incapable of paraquat adsorption, although cation exchange resins were well-suited to its removal. A number of compounds were tested and, the order of adsorption efficiency was CIPC > trifluralin > 2,4-D > diphenamid > DNBP > Amiben.

Studies with various phenylamide pesticides showed rapid and efficient adsorption by powdered activated carbon (El-Dib and Aly, 1977b). Again, adsorption conformed to a Freundlich isotherm and equilibrium conditions were found to be established within 15 minutes of initial contact. Adsorption for the phenylcarbamates followed the order: CIPC > IPC, for the phenyl ureas the order was: diuron > linuron > neburon > monuron > fenuron, and for the anildes: Karsil > Stam > Vitava. The general solubility/adsorbability pattern was followed here as well. Adsorption was affected by steric hindrance, such as those arising from the extended side chain of neburon or the "bulkiness" of the Vitavax molecule. Further studies by Sigworth (1965) showed the amenability of some organophosphate and chlorinated insecticides to activated carbon treatment. Results are summarized in Table 11.

Table 11. Carbon adsorption of organophosphate and chlorinated insecticide

Pesticide	initial conc. (mg/L)	final conc. (mg/L)	carbon dose (mg/L)
parathion	10	2.6	10
malathion	25	.08	5
lindane	2	.25	10
2,4-D 23.5%	6	1.38	20
2,4-D 11.7%	1	*	10
chlorodane	50	*	10
DDT	5	*	2

Eichelberger and Lichtenberg (1971) demonstrated the efficiency of activated carbon in "scrubbing out" low concentrations or organophosphate pesticides by column application. Bidrin, ethion, azodrin, parathion, fenthion, DEF, trithion, malathion, and methyl-parathion were all reduced from 3 mg/L (ppb) to less than 25 mg/L (ppt) by passage through a lab scale column. A number of chlorinated compounds were reduced to levels less than 10 ppt.

El-Dib et al. (1973) used a 0.6/mm and 1.2/mm Dcro granular activated carbon to determine the adsorbability of two carbamate insecticides, carbaryl and baygon in both batch tests and down-flow columns. The results were shown to follow both Fruendlich and Langmuir isotherms. Monolayer capacity for carbaryl was found to be 800 moles/g on 1.2/mm granules and 1250 moles/g for the 0.6/mm size. Capacity was independent of particle size for Baygon. Both sizes had a capacity value of about 500 moles/g.

For column operation, contact time was a critical parameter. Increasing the contact time from 0.5 to 3.75 minutes (influent carbaryl concentration of 20 mg/L) increased the number of bed volumes passed before breakthrough (chosen as 0.1 mg/L) from 15 to 425. The effect was nearly as remarkable for Baygon, which showed almost immediate breakthrough at the 0.5 minute contact time while 273 volumes were successfully treated during a 3.75 minute contact. At the higher contact time, almost complete adsorption capacity was realized, independent of bed depth.

El-Dib et al. (1973) stated that the difference in the adsorption behavior of the two pesticides could be explained by molecular structure differences. The side chains of the carbaryl molecule all lie within the same plane, while the 2 methyl groups in the isopropyl chain of baygon lie in a different plane with respect to the ring. Hence, steric hindrance in entrance into the carbon micropores may have resulted, along with the fact that the molecule may have had weaker adhesion to the carbon because of lower surface coverage and attachment area.

Based on these studies, especially those that illlustrate the great effectiveness of carbon for the removal of organophosphates and various nitrogen containing pesticides, it appears that activated carbon represents a viable treatment alternative for field disposal systems. Additional advantages include the ability to remove most chlorinated compounds, along with the fact that carbon adsorption appears to be applicable for achieving the goal of water reuse, since a high quality effluent is obtainable. The broad applicability, economy, and efficiency of this treatment method present distinct advantages not found in any other treatment schemes.

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SECTION 5

5. SAFETY CONSIDERATIONS

Individual safety is of primary concern in handling pesticides or pesticide contaminated waste. Pesticide toxicity is often compared on the basis of LD_{50} (the amount of material in mg per kilogram of body weight, that will result in the death of 50 percent of the test animals). Dermal toxicity is of equal or greater practical concern for the pesticide applicator or treatment plant operator. This is especially true in cases where organophosphate pesticides, that are easily absorbed through the skin, are involved. Comparisons of oral and dermal toxicity data are given in Table 12. The risk of oral poisoning can, of course, not be neglected and the standard safety procedures of not smoking, eating or drinking when handling these chemicals should always be observed.

It should be noted that any treatment system containing open tanks, pumps and hosing is susceptible to leaks, gasket failures, vapors, and spillage. This is especially true for hose connections that, when periodically operated under conditions of moderate to high pressure, may separate and leak. As a result, the following safety procedures were recommended for the operation of the designed pilot plant.

1. Employees should never work alone

2. The treatment plant should be kept in a well ventilated area

3. The treatment plant should be enclosed to maintain equipment life and minimize runoff

4. The area around the treatment system should be diked and, if possible, a sump pump should be installed to collect spills

5. Only individuals experienced in the handling of pesticides should be in charge of plant operation

6. The operator should be aware of the usual symptoms of pesticide poisoning. These symptoms include headache, giddiness, nervousness, blurred vision, weakness, nausea, and cramps. Signs of poisoning include profuse sweating, tearing, salivation and other excessive respiratory tract secretions, and vomiting. In later stages, cyanosis, papilledema, uncontrolled muscle twitches, convulsions, coma, loss of reflexes, and loss of sphincter control may occur.

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Table 12. Toxicities of Selected Organophosphate and Carbamate Pesticides

Label Accepted Common Name	Some Trade Names	Acute Oral LD_{50} mg/kg*	Acute Dermal LD_{50} mg/kg*	Purchase Permit Required
phorate	Thimet	2.3	3-6	Yes
dementon	Systox	2.56-6.2	8-14	Yes
none	Di-syston	2.3-6.8	6-15	Yes
none	Phosdrin	3.7-6.1	4-5	Yes
none	Sulfotepp, Dithio	5	8	Yes
none	Dasanit	2-11	3-30	Yes
ethyl parathion	Thiophos, Orthophos, Phaskil	3-13	7-21	Yes
none	Guthion	11-13	220	Yes
none	Dyfonate	16	319	Yes
methyl parathion	Dalf, Metron	14-24	67	Yes
carbophenothion	Trithion	10-30	27-54	Yes
none	EPN	8-36	25-230	Yes
phosphamidon	Dimecron	23.5	107-143	Yes
none	Co-Ral	9	860	Yes
dioxathion	Delnav	23-43	63-235	Yes
ethion	Nialate	27-65	62-245	Yes
famphur	Warbex	35-62	1460-5093	Yes
DDVP	Vapona	56-80	75-107	Yes
none	Meta-Systox-R	65-76	250	No
none	Diazinon	76-108	455-900	No
none	Methyl Trithion	98-120	190-215	No
none	Ciodrin	125	385	No
phosalone	Zolone	82-205	2000+	No
none	Dursban	97-276	2000	No
none	Imidan	147-216	3160	No
dimethoate	Cygon, De-Fend, Rogor	215	400-610	No
fenthion	Baytex	215-245	330	No
naled	Dibron	250	800	No
	Neguvon	560-630	2000+	No
malathion	Cythion	1000-1375	4444+	No
ronnel	Korlan, Trolene Nankor	1250-2630	5000	No
carbofuran	Furadan	8.1-14.1	885	Yes
methomyl	Lannate	17-24	1500+	Yes
none	Zectran	25-37	1500-2500	Yes
none	Dimetilan	64	600+	No
none	Baygon	95-104	1000+	No
none	BUX	7	400	No
carbaryl	Sevin	500-850	4000+	No

* The range in LD_{50} numbers is due to differences in susceptibility between male and females, between different strains of test animals, and between different carriers of the pesticide.

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7. A change of clothing and, if possible, shower facilities should be nearby. Clothing should always be washed (but never with the family wash) before re-wearing.

The chemicals required for treatment plant operation should be handled carefully. Although aluminum sulfate (alum) is not considered a particularly hazardous chemical, its acidic action can cause irritation of eyes, skin, and mucous membranes. Sodium hydroxide is highly corrosive while polymer solutions, although not irritating to exposed areas, are usually viscous and slippery and can be dangerous, if spilled. Consequently, the following procedures are recommended:

1. Only relatively small volumes of chemicals should be transferred at any one time.
2. Volume measurement should be done away from the treatment facility.
3. Soap and water should be on hand for washing and flushing of skin and eyes.
4. Plastic labware (graduated cylinders, beakers, etc.) should be used to minimize the hazards of breaking glass.

In order to minimize personal risk, the following safety equipment should be worn at all times when handling pesticides. Note that most household gloves deteriorate when handling organophosphates and, therefore, should not be used. Wearing of leather shoes is discouraged. This list of safety equipment is adapted from Lande (1978) and is applicable to all individuals who handle pesticides.

1. Impervious or rubber head covering.
2. Protective eye goggles (preferred) or safety glasses.
3. Organic vapor respirators — cartridge type, as approved by U.S. Department of Agriculture
4. Washable work clothing.
5. Natural rubber gloves.
6. Latex rubber apron, ankle length (for plant operation) or rain suit for outside washing operators.
7. Rubber workshoes or overshoes.

SECTION 6

REVIEW OF EXISTING PRACTICES

In order to obtain more information concerning pesticide disposal problems encountered by commercial pesticide applicators around the country, State Aviation Associations were contacted. Information from 36 agencies is shown in Table 13. This table identifies the regulatory agency that is responsible for registration of aerial applicators, the registration requirements, any problems encountered by applicators in the hauling or usage of pesticides, and the types of pesticides commonly used in each state. Ten states indicated that aerial applicators face several specific problems. A range of problems range were mentioned, including spillage during loading and unloading, runoff from the site, container disposal, and collection of pesticide wastewater. The state of Nebraska indicated that pesticide applicators are required to contain all wash and rinse water used in cleaning pesticide application equipment. The collected wastewaters are treated either with acid or alkali to hydrolyze the pesticide before disposal.

Some states, specifically California, require closed-loop mixing systems for the loading of pesticide application equipment. This type of system minimizes the problems associated with container disposal and spillage during the loading and unloading operations. However, the closed-loop system does not eliminate the need for a system to treat the wastewater generated when the application equipment is cleaned.

In addition to contacts with state regulatory agencies, numerous aerial applicators have been interviewed. Most of these applicators describe two basic problems. First, many operate at several airport locations. Normally, any large application that requires more than one load of pesticides and is located more than 16 Km (10 miles) from the operator's airport will be serviced from a private landing strip. These small landing strips are isolated and have no cleaning facilities. The pesticides are usually mixed on a service truck and then pumped into the application equipment. Occasionally, the application equipment is rinsed out at these remote locations, although normally the cleaning of the aircraft occurs at the central airport location.

The second major problem is the large, fixed capital cost required for treatment facilities. Most of the applicators are unwilling to depreciate a facility over a 5-year period, since their longevity at a particular location is unknown. Most of the applicators do not own the airport and are working on a yearly lease basis with the local airport authority and, hence, the question of who should be responsible for any large capital outlay is of great concern.

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These responses from the regulatory agencies and from the applicators indicate that there is a great need for a coordinated effort in the development of the pesticide collection system. The state regulatory agencies must be made aware that this is a problem faced by all applicators. They must be willing to work with applicators in order to insure that the cost of the collection and treatment system is equitably distributed between the pesticide applicator and his/her clients. In addition, the implementation of closed-loop mixing and transfer system should be emphasized, because this system eliminates the spillage problem during the mixing and transfer of pesticide solution and thereby greatly reduces the need for the collection system at each of the remote locations that the applicator may use so long as the applicators avoids cleaning his/her equipment at remote locations. All of the waste pesticide, wash, and rinse water from the application equipment should be collected at a central location.

Since most of these criteria are currently in the form of proposed or implemented regulations either from state or federal government agencies, it would appear that it is only a matter of time before there will be a uniform policy across the country for the collection and containment of the pesticide wash water.

Table 13. State Regulations Affecting Aerial Applicators

STATE	REGULATORY AGENCY	REQUIREMENTS OF REG.	PROBLEMS	ORGANIZED GROUP	PESTICIDES USED
AL	Comissioner of Ag & Industries	written exams premises, license	spillage in loading & unloading	AL Ag. Aviation Ass'n.	
AK	Bureau of Land Mgmt.		None	None	
AR	State Plant Board	permit, records, license		AR Ag. Aviation Ass'n.	Endrin, toxaphene, chlordane, thiodan, 2,4-D; 2,4-T
AZ	Board of Pesticide Control		rinse container Aviation adding rinsates to mix tanks	AZ Ag. Ass'n.	numerous
CA	Dept. of Food & Ag	exam, records	yes	AG Aircraft Ass'n.	
CT	Pesticide Compliance Unit of the CT Dept. of Envir. Protection	permit	None	None	Carbaryl, malathion methoxychlor, diazion, thiodan, naphthaleneacetic acid, cygon, captan, maneb-zineb 2,4,5-T, polygram ferbam, metasystox R, difolatan, casoron granular
DE	Dept. of Ag.		None	None	numerous
FL	Dept. of Ag. & Consumer Services		None	None	Carbaryl, lannate benlate, mocap, CDEC, sulfur
GA	Dept. of Ag.		None	GA Ag.	Bravo, duter, benlate, def, folex, paraquat, dynap, dynitro, 6-3 mix, atrazine, toxaphene, methyl parathion, azodrum, methomyl

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Table 13. (Continued)

HI			None	None	Urea, ammonium phosphate, TSP super phosphate, potash, polaris, paraquat, amatrine, DCMU, weed killers, dalapon, atrazine, gibberilic acid
IL	Dept. of Ag.				
IN					
KY	Dept. of Natural Resources & EPA		None	KY Ag. Aviation Assn.	Paraquat, benlate, parathion, sevin, lannate, malathion
ME			None	None	Tordon 101, captan, guthion, sistox, cyprex, pollyram
MD		None	None	None	Unknown
MA			None	None	Parathion, systox, guthion, various herbicides,fungicides, bisdithiocarbonates, methylmyl, lannate, carbaryl, malathion, abate, chloropyrofs, methoxychlor
MI	Dept. of Ag.		None	Aviation Ass'n.	parathion, atrazine, dinitrol, monitor
MS	Ag. Aviation Board	license exam, residency	disposal of unused containers	MS Ag. Aviation Ass'n.	most used for cotton, soybeans, & rice
MO	Dept. of Ag.		yes	MO Aerial Applicators Ass'n.	most herbicides & most all herbicides
NH	Dept. of Ag.		None	None	Malathion, tordon 101, lannate,manzate,sevin, thiodan, dipel, abate, 2,4,5-T; methoxychlor

Table 13. (Continued)

NJ	Dept. of Envir. Prot.	exam, permit, records	None	N.E. Ag. Aviation Ass'n.	Many
NM	Dept. of Ag.		Used pesticide containers		Primarily carbamates & organophosphates & toxaphene
NY			None	None	
NE	Dept. of Aeronautics	exams	Concrete applicator aprons are used for loading & unloading	NE Aviation Trades Ass'n.	Carbaryl, furidan, parathion, atrazine, disyston, banuel, 2,4,5-T; 2,4-D; tordon,sulfur,ramrod, bladex
ND	ND Aeronautic Commission		spillage; failure to clean out when changing	ND Aviation Ass'n.	Numerous
OK	Dept. of Ag.		None	J.L. Putnam	
OR	Dept. of Ag.		None	OR Aviation Trade Ass'n.	Pesticides & fertilizers
PR	FAA		None	None	Diazinon, dipel lannate
SC	SC Aeronautic Commission	permit	None	SC Ag. Aviation Ass'n.	
SD	Dept. of Ag.		Runoff; vapor drift	SD Aviation Trade Ass'n.	2,4-D; sevin,larathion, dicamba, malathion, superacide
TN	Dept. of Ag.		None	TN Aerial Applicators Ass'n.	methyl parathion,lasso, lannate, treflan, 2,4-D; paraquat toxaphene, galacron fundal
UT			None	None	Parathion, mitasystox, dursban, diazanon, disiston

Table 13. (Continued)

VA		None	VA Pesticide Ass'n.	
WA	Dept. of Ag	yes	Ag. Applicators	Dessicants, phenoxy-Hormone type; banvel, phosdrin, phosvel, parathion, methyl parathion, sevin, lannate, linidon, diazinon
WI		None	Reabe Flying Service	Parathion, paraquat, dithene, sevin
WY	Dept. of Ag.	None	None	2,4-D; malathion, parathion, sevin

SECTION 7

CLEANUP AND COLLECTION SYSTEM

In order to implement a control system for treating the wastewater that is generated when application equipment is washed, a cleanup and collection system must be designed. In the preliminary phases of this project a portable system was used to collect wastewater samples for analysis and characterization of the wastewater. This portable collection system consisted of a 12.2 m x 13.4 (40 ft. x 44 ft.) vinyl sheet, which was spread under the application equipment. After the aerial application equipment was washed the wastewater was diverted to one corner of the sheet, and pumped into appropriate containers. A high pressure sprayer was used for the washing of the aircraft. A boiler on the high pressure sprayer made it possible to use hot water for cleaning both the pesticide application system and the surface of the aircraft.

This collection system was first taken to the Southern Crop Service at Del Ray Beach, FL where it was used to collect samples from aircraft as shown in Figures 1. Samples were taken from the residue left in the application equipment, wash and rinse water from the pesticide spraying system and wash water from the surface of the plane. Approximately 25 gallons of water were needed to clean the spray systems on these planes. Results of the analysis from these various samples is reported in Section 8.

Although the portable system was useful in collecting the initial samples, the amount of labor required to divert the wastewater to the corner of the vinyl sheet was too great for use in a practical treatment collection system. As a result, a permanent modification was made to an existing pads at the Garwood Airport in Monon, IN. This installation is shown in Figures 2 and 3. The existing concrete pad had previously been crowned so that the pad would drain to the gravel pit located around the outside perimeter. A diversion was built around the outside of the concrete pad to collect and channel the water to one corner, where a small sump was constructed and a submersible sump pump was installed. The wash and rinse water was pumped into a 3790 L (1000 gal.) storage tank that was located on the site. This system worked quite well and allowed for the continuous collection of wash and rinse water from the aerial applicator.

Experience with the system has shown that it is unnecessary to segregate the wastewater into separate fractions. Although the concentration of pesticides is highly variable, the treatment system developed is capable of handling these variations. The complexity of segregating the wastewater into fractions of decreasing concentration would complicate the system

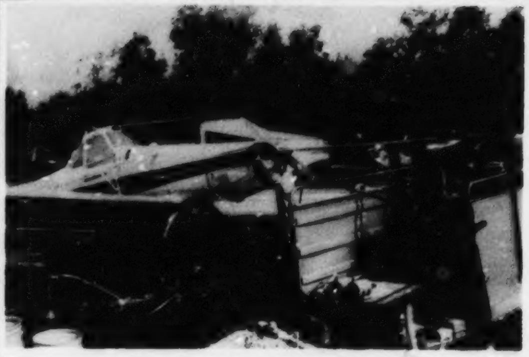

Figure 1. Vinyl sheet used to collect wash water from aircraft in initial phases of study.

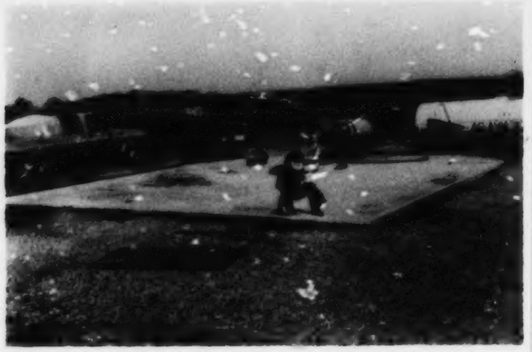

Figure 2. Concrete pad at pesticide mixing area at Garwood Airport in Monon, Indiana.

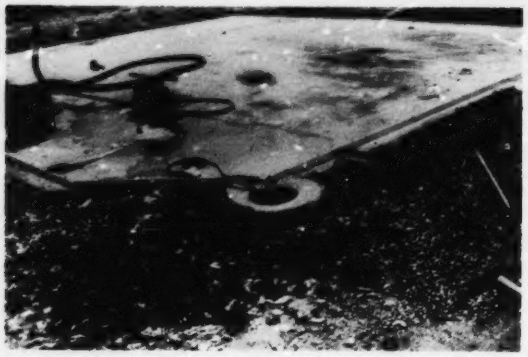

Figure 3. Modification in collection pad included installation of a sump and diversion of all wash water to one corner of the pad.

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unnecessarily. All of the wash water, rinse water, and excess pesticide formulation can be dumped onto a concrete pad and drained into a central sump. This same pad could be used for mixing and loading of the application equipment. This technique would insure that all of the pesticide contaminated waste would be contained and could be treated with the proposed system.

Two alternative techniques for the collection and storage of the pesticide-contaminated wash water would be possible. One alternative would be to install and underground tank directly below the pad. This underground system would provide the "neatest" appearance for the applicator. However, there are several problems associated with below grade storage. Sludge accumulation in the bottom of the tank could be difficult to remove and leaks in the tank could go unnoticed for a period of time and result in significant groundwater contamination. Earth excavation and tank placement would represent a sizable fixed investment for the operator with limited salvage value if the applicator moves to a new site.

An above ground tank would eliminate several of these problems. Sludge accumulation in the bottom of the tank could be easily prevented by mixing and flushing from the tank. Any leakage would be readily noticeable and correctable. Further advantages of above ground storage are lower cost, along with greater flexibility in location of the storage structures. Two notable disadvantages would be that such a storage tank could interfere with traffic around the collection pad and that a pump would have to be used to move wastewater from the sump to the above ground tank.

Some safeguards should be provided to prevent rain water from entering the collection system since this would increase the volume and dilute the wastewater to be treated. Although the treatment plant is capable of handling a wide variety of wastewater concentrations it is always preferable to minimize the volume treated. A cover over the collection pad is recommended. Such covers are readily available for covering athletic fields and could be easily implemented on a relatively small-scale.

At this time, it appears unnecessary to have the collection pad enclosed in a building. Enclosures would inhibit the accessibility of the pad to the applicator for the filling and mixing of pesticides. The applicators who have evaluated the system concur with this opinion and would prefer to use an open pad. The drift of pesticides away from the pad does not appear to be a significant problem. This system could be employed on most currently existing applicators' facilities. The cost of such a system is projected in Section 10. The success of the treatment system requires a simple and inexpensive method of collecting the wastewater.

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SECTION 8

LABORATORY STUDIES

Data is extremely limited on the concentrations and amounts of pesticide-contaminated wash water generated during the cleanup of agricultural aircraft. In fact, since there are no standardized cleaning or disposal procedures for this industry, the problem of finding reliable data is compounded.

8.1 WASTEWATER CHARACTERISTICS

Faced with such a lack of information, the investigators in this project felt that the only viable alternative for obtaining relevant data was to visit an actual site. Approximately 758 L (200 gal.) of wastewater and rinse water were collected at the Southern Crop Service Headquarters in Del Ray Beach, Florida. Samples were drawn from a number of sources including tank drainage, rinse water, and wash water. A high pressure sprayer was used to wash both Piper Pawnee and Weatherly Ag Tractor aircraft. Dry powders or dust and liquid formulations were obtained. In addition, samples were taken from an on-site holding pond that had been used for the storage of pesticide wastewater for several years.

Because of the highly mixed nature of the waste, analyses were limited to gross parameters such as COD, pH, and solids determination. During the initial stages of the study there was no necessity of determining specific pesticide concentrations.

The samples from Southern Crop Service were returned to West Lafayette, IN for analysis. Analytical data and source information are summarized in Table 14. Samples designated as A were obtained by direct drainage of excess pesticide left in the plane hoppers after spraying had been completed. The A-1 sample contained parathion, M-75 fungicide and 20-20-20 foliage fertilizer, while sample A-2 contained toxaphene, lannate, 20-20-20 foliage fertilizer, A-3 contained M-75 fungicide, parathion and lannate while A-4 contained thiodan, guthion and M-75. Samples designated at "B" were taken from the on-site, earthen holding pond. Sample "C" was pumped from an on-site well used to provide wash water. Samples D-9 thru D-16 were taken from a Pawnee aircraft after it had finished spraying a solution containing M-45, nutri-leaf cygon, toxaphene and parathion. All other D samples were taken from another airplane spraying a solution containing 57 L (15 gal.) of Toxaphene, 38 L (10 gal.) of phosdrin, 38 L (10 gal.) of cygon, 91 Kg (200 lbs.) of urea, 23 Kg (50 lbs.) of M-45, 9.5 L (2.5 gal.) parathion, and 9.5 L (2.5 gal.) lannate. The "E" samples were drawn from a Weatherly ag tractor that had sprayed a

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solution of M-45, dithane, methyl-ethyl parathion, toxaphene, nutri-leaf, and 20-20-20 foliage fertilizer.

Table 14. Characteristics of Wastewater Samples Collected in Florida

Sample	Source	COD Total	COD Sol.	pH	TSS	SVS
A-1	Tank drainage	81,500				
A-2	Tank drainage	59,000				
A-3	Tank drainage	66,600				
A-4	Tank drainage	23,500				
B	Holding lagoon	6,700				
C	Well water	45				
D-1	First rinse-pesticide tank (after 15 gal.)	375	189	7.3	130	85
D-2	First rinse-side loading lock	3,000	2,326	7.4	950	
D-3-D-8	Aircraft surface wash	1,200	500	7.5	600	350
D-9-D-15	Aircraft surface wash	1,200	500	7.5	600	350
	with detergent	750	200	7.5	550	300
D-16	Detergent wash with bottom sediment	3,000	1,048	6.7	3000	1,000
D-17	Bottom first rinse	40,000	25,500	7.1	2,100	1,600
E-1	Initial tank rinse water	55,000	16,800	6.0	24,000	19,400
E-2	Last of first rinse water	8,000	5,130	7.4	7,000	
E-3	Last of first rinse water	8,500	5,020	7.0	18,000	14,000
E-4	First rinse-side loading rack	14,000	6,454	6.4	5,400	4,200
E-5	First rinse boom	13,000	9,600	6.5	11,600	8,900
	(Note following samples taken at 5 gal increments)					
E-6	Third rinse boom	3,500	650	6.8	3,200	2,300
E-7	Fourth rinse boom	2,000	205	6.8	1,000	980
E-8	Fifth rinse boom	450	166	7.4	110	90
E-9-E-11	Composite	1,200	904	6.9	1,140	950

Because samples D and E represented the type of waste that would be treated by our proposed facility, a more thorough analysis was performed. COD determinations along with pH, total and volatile suspended solids were sufficient to adequately characterize the waste for the proposed treatment system. An attempt was made to determine total solids on several samples, but pungent fumes were released into the laboratory due to the high volatility of the waste. The total solids determinations were discontinued for safety reasons.

All samples, with the exception of C, were noted for a striking greenish-yellow color along with a sizeable amount of settleable material, forming a "mud" on the bottom of the sample containers.

These collected samples covered a wide range of solids concentrations, while the pH was relatively consistant with values in the range of 6.4 to 7.5. The composite sample of the wash and rinse water collected provided the most realistic sample of the wastewater. These samples, D-3 through D-15 and E-9 through E-11 had a COD of approximately 1000 mg/L. Consequently, a pesticide concentration sufficient to give a chemical oxygen demand of approximately 1000 mg/L was used for initial lab scale testing of various treatment alternatives.

8.2 LAB EVALUATION OF WASTE WATER TREATMENT TECHNIQUES

The representative sample, E-9 through E-11 was used for initial lab testing. Approximately 57 L (15 gal.) of this sample were available, so a wide variety of tests were performed.

Due to the high suspended solids content of the waste (approximately 1100 mg/L). Preliminary coagulation/flocculation/sedimentation procedure were used to reduce the COD concentration. A series of tests was set up to analyze the effects of coagulant types and dosages.

First, sodium hydroxide was tested as a flocculant. The dosages were adjusted so as to cover a range of pH values. Here, as in all further testing, samples were rapidly mixed for two minutes, slow mixed from 10 to 15 minutes to promote particle agglomeration, and allowed to settle for 25 minutes. Floc characteristics were noted and the efficiency of the operation was measured by determining the COD of the supernatant. A summary of the data is present in Table 15.

Table 15. Hydroxide Coagulation of Wastewater Samples Collected in Florida. Initial COD was 1200 mg/L.

pH	Final COD	Floc Characteristic
9.0	360	Very Turbid
10.5	260	Very Turbid
11.6	262	Slightly Turbid
12.2	271	Slightly Turbid
12.6	292	Clear
12.9	327	Clear

Alum was also evaluated as a coagulant. It should be noted that the efficiency of alum coagulation is dependent on whether there is sufficient alkalinity in the wastewater to allow formation of the aluminum hydroxide precipitate. Alkalinity determinations on sample E-10 and the well water gave identical values at 273 mg/L as $CaCO_3$. Sufficient alkalinity was present to react with dosages of alum up to 200 mg/L. A summary of the alum flocculations data is presented in Table 16. The final pH of the treated solutions were between 6 and 8, the effective range for alum coagulation.

Table 16. Alum Coagulation of Wastewater Samples Collected in Florida. Initial COD was 1200 mg/L.

Alum (mg/l)	Final pH	Final COD	Floc Characteristics
50	6.9	352	Turbid
100	6.6	318	Clear
150	6.4	322	Clear
200	6.4	286	Slightly Turbid
250	6.3	306	Turbid
300	6.1	300	Turbid

Based on these studies, hydroxide coagulation was most effective at pH 11, while optimum alum dosage was around 200 mg/L.

Ferric chloride was also evaluated as a coagulant and results were very similar to those of alum. The degree of COD removal was found to be independent of pH in the range of 4.3 to 8, as might be expected from the wide effective pH range of the iron salts, and supernatant COD values were essentially the same as those for alum at equivalent coagulant doses. The quality of the supernatant measured in terms of COD did not correlate with the visual appearance of the samples. Part of the reason for this phenomena may have been due to the fact that percentage differences between COD values were small and are not significant in light of the errors inherent within the COD procedure.

Solutions of carbaryl and malathion prepared in the laboratory were also evaluated. Tests showed that carbaryl dosages of 500 mg/L and malathion volumes of 5 ml/L produced COD values closely approaching those found for solutions E-9 through E-11, these solutions were used for all further laboratory equation studies. A pH of 11 was again found to be optimum for hydroxide coagulation. The results of flocculation/cougulation studies on these synthetic solutions are summarized in Tables 17 and 18.

Table 17. Hydroxide Coagulation of Malathion

pH	Initial COD	Final COD	% Removal	Floc Characteristics
10	671	285	57.2	Turbid
10.8	684	269	60.7	Clear
11.8	669	375	44	Clear with floating solids
12.3	605	384	37	Clear with floating solids
12.6	676	431	36	Clear with floating solids

Table 18. Hydroxide Coagulation of Carbaryl

pH	Initial COD	Final COD	% Removal	Final Characteristics
8.5	-	-	-	No effect
9.3	-	-	-	No effect
10.1	660	567	14	Turbid
11.2	663	360	45.7	Slightly turbid
11.9	636	360	43	Very clear
12.3	650	373	42.6	Very clear

Tests using alum on synthetic solutions produced similar results, that is, approximately 200 mg/L of alum were required to obtain maximum COD removal. Only minor differences in COD removal occurred with alum dosages of 100 to 300 mg/L.

Test solutions were filtered to compare filtration to flocculation and settling. A carbaryl solution of 831 mg/L was filtered through Whatman #1 filter paper (11 μ pore size) to produce a solution with a COD of 200 mg/L, giving a 75 percent COD removal, slightly better than the removals observed during flocculation. Filtration of malathion solutions only reduced COD from approximately 920 mg/L to about 700 mg/l, indicating that these emulsions cannot be successfully treated by filtration.

The next step in the laboratory study was to evaluate activated carbon adsorption. Five different brands of carbons were received from three manufacturers, and each was evaluated for its ability to remove carbaryl and malathion. This evaluation was performed by conducting isotherms studies for each carbon. Different amounts of carbon were added to 100 mL, of the sample.

Samples were placed on a shaker table and allowed to equilibrate for two hours. All pesticide solutions for the isotherm studies were prepared by first flocculating the samples with either sodium hydroxide or alum and then filtering through a millipore filter. Carbon was then added and after the 2 hr. equilibration, the carbon was removed by filtration through a millipore filter.

A graph of the data according to a Langmier equation is provided were q_e is equal to the milligrams of pesticide (expressed as COD) adsorbed per gram of carbon and represents the final equilibrium concentration of the pesticide. The carbon giving the line with the least slope is the best adsorbent.

Figures 4 and 5 show that the Darco HD-3000 is the preferred adsorbent for carbaryl, and that the hydrolysis that occurs from hydroxide coagulation produces a more readily absorbed product. This result is suprising in light of the findings of other researches. However, the situation is quite different with malathion as is illustrated in Figures 6 and 7. The alum flocculated effluent is adsorbed more efficiently than the hydroxide products, and that the Nuchar WV-L 12 x 40 mesh is the better adsorbent. Other isotherm studies were run of Filtrasorb 400, and it was found to be inferior to the Nuchar WV-L for all cases although the isotherms were fairly close for the alum coagulated malathion as shown in Figure 8.

At this point, a decision had to be made as to which carbon to use in the pilot plant. Unfortunately, this decision was not clear. The best carbon for carbaryl removal was not best for malathion removal. The carbon contact unit was designed for malathion removal. The basis behind this decision was that carbaryl is more amenable to removal by pretreatment filtration or coagulation since it is used preliminary as a solid formulation. Therefore, maximum life of the carbon bed could be achieved by maximizing malathion removal.

In order to test the isotherm data, column studies on the removal of malathion were begun with Nuchar WV-L 12 x 40 mesh carbon and Filtrasorb 400. Two six-inch high, 1-inch diameter columns were constructed and fed flocculated and settled malathion solution at a rate of 1.4 L/s-m^2 (2 gpm/ft.^{2}).

For the Filtrasorb, leakage of 3-5 mg/L COD appeared immediately, and this increased to 20 mg/L after 12 liters, about 20 mg/L after 30 liters, 30 mg/l after 36 liters and so on as shown in Figure 9. Operation of the column stopped at 71 liters, where the COD concentration reached 140 mg/L. It should be noted that the feed solution had a COD of 220 mg/L.

For the Nuchar carbon, better results were obtained, as predicted by the isotherms. No significant leakage occurred until almost 30 liters had passed through the column. Nearly 44 liters passed before 5 mg/L COD was found in the effluent. This response is also illustrated in Figure 9. The column was shut down after 142 liters had passed with an effluent COD of 105 mg/L.

The capacity of the Nuchar before breakthrough (chosen to be 5 mg/L) was calculated to be 220 mg COD/gram carbon. At 10 percent breakthrough (20 mg/L) the capacity of the carbon was approximately 360 mg COD gram carbon, a very favorable degree of adsorption.

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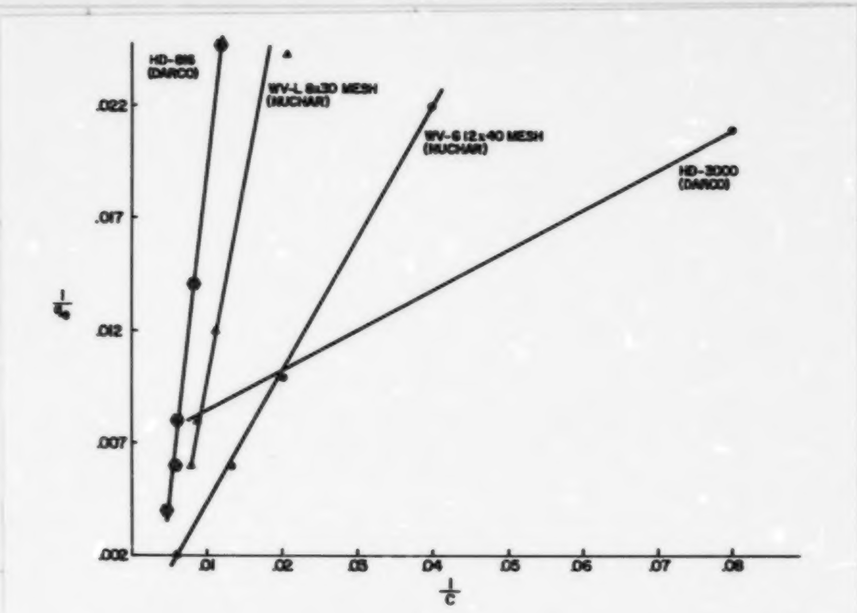

Figure 4. Langmuir Isotherm plots of the adsorption of carbaryl following alum coagulation.

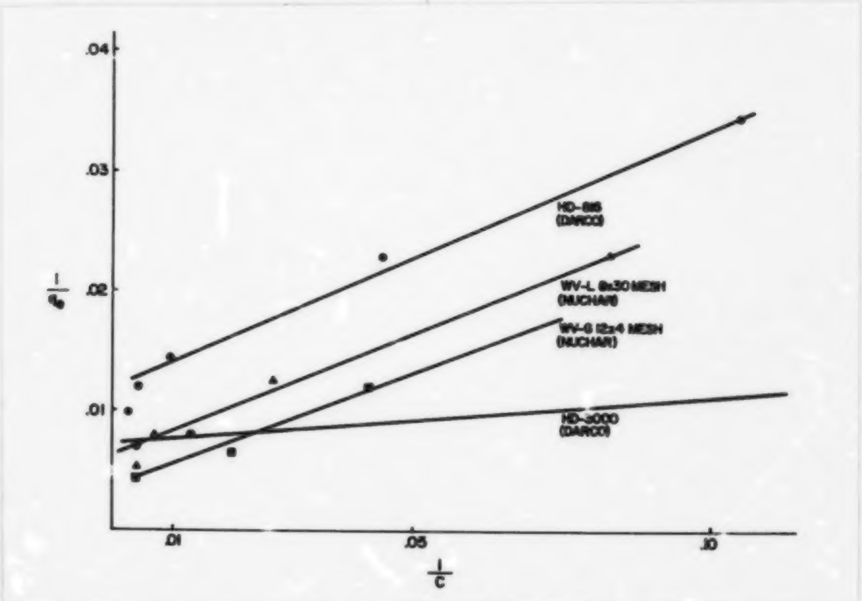

Figure 5. Langmuir Isotherm plots of the adsorption of carbaryl following hydroxide coagulation.

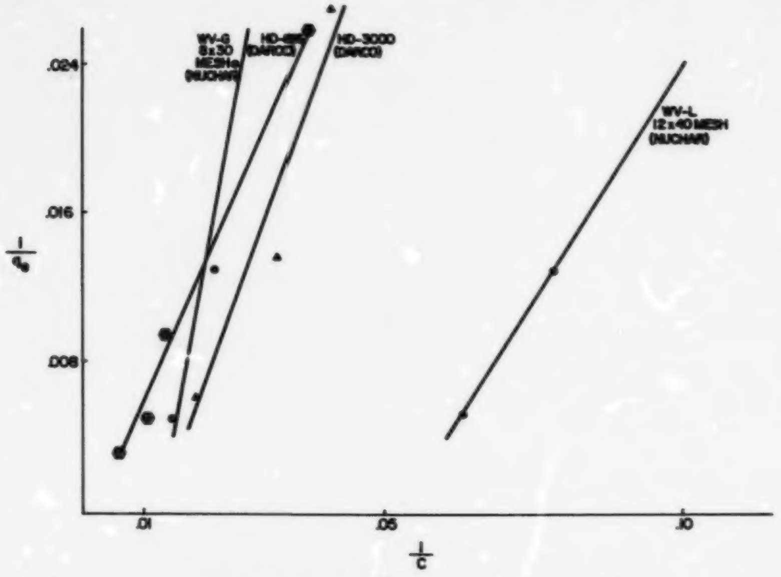

Figure 6. Langmuir Isotherm plots of the adsorption of malathion following alum coagulation.

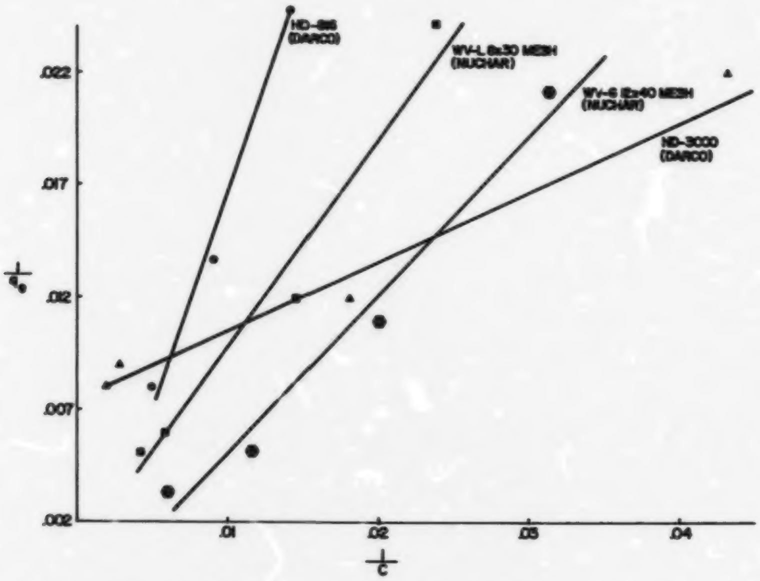

Figure 7. Langmuir Isotherm plots of the adsorption of malathion following hydroxide coagulation.

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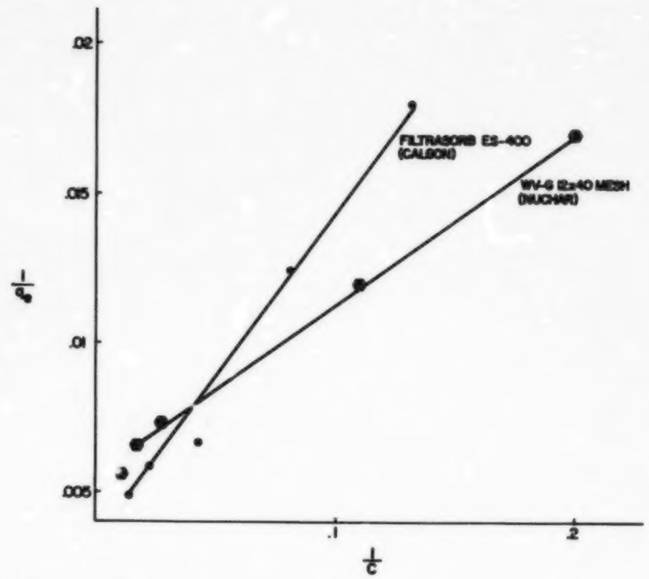

Figure 8. Langmuir Isotherm plots of the adsorption of alum coagulated malathion samples on Filtrasorb-400 and WVG.

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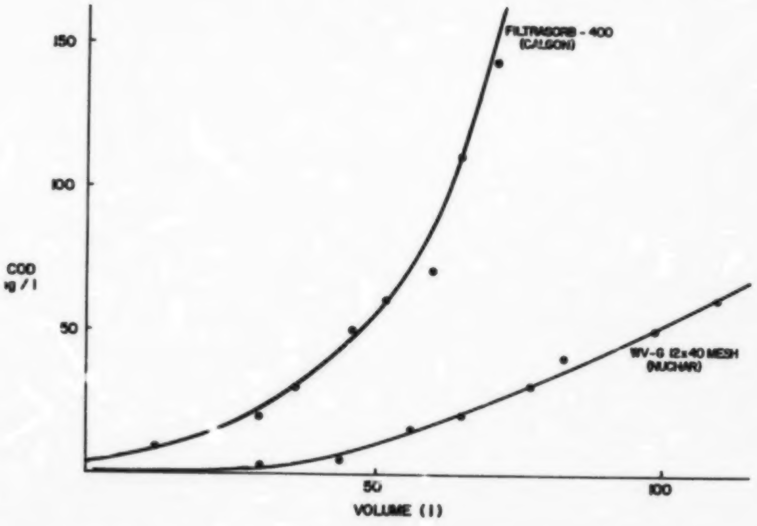

Figure 9. Carbon adsorption of malathion on columns of Filtrasorb-400 and WVG.

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Based on these results, a pilot plant with an initial filtration, followed by flocculation and settling, followed by coalescence and carbon adsorption should provide good removal for both carbaryl and malathion. In the pilot plant both Filtrasorb and Nuchar carbon were used to provide further comparisons of adsorption efficiency.

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SECTION 9

PROTOTYPE SYSTEM

The pilot treatment plant was designed to analyze the effect of various treatment options on the removal of pesticides from actual and synthetic wastewaters generated by pesticide applicators. Based on the success of several treatment options in the laboratory, both coagulation / flocculation/sedimentation and activated carbon adsorption were included in the final design. Filtration and oil coalescence were added to the pilot plant since these processes are phase separation procedures fundamentally similar to coagulation/flocculation, and presented possible advantages in overall convenience of operation. The system was designed to be a collection of unit operations. All connection between these individual units were made by flexible hose with screw-type fittings. This arrangement allowed for evaluation of various sequences of unit operations. A schematic diagram of the system is presented in Figure 10.

The pilot plant (Figure 11) was tested in both field generated and synthetic pesticide solutions. Solutions derived from field washing operations were collected (collection system is described in Section 7) and pumped to a 1890 L (500 gal.) holding tank secured on the bed of a small truck. These field generated samples were returned to the Agricultural Engineering building at Purdue University, where it was transferred to holding tanks. These holding tanks also served as a reaction vessel for the first unit operation of coagulation/flocculation/sedimentation.

The filtration systems were tested for their efficiency in the removal of suspended solids. Two of the systems, a Cuno cartridge filter and the Ronnigen-Petter fabri-basket filter were chosen for their operating convenience and for the wide range of pore sizes available. The Cuno filter consisted of a diatomaceous earth type cartridge seated in a stainless steel housing. Cartridges with filtration pore size of 25 and 5 microns were chosen for study and are shown in Figure 12. The second filtration unit, the fabri-basket filter consisted of a nylon "sock" fitted into a perforated metal basket support. Again, media of different pore size are available, although the 1 micron size was chosen for this research (Figure 13).

Despite the fact that these two units were considered to be adequate for the removal of solid formulations, such as dusts or granules, they cannot be expected to be effective against emulsified formulations. Consequently, a Balston filter tube coalescer, consisting of a hollow fiberglass type tube supported within a clear plastic housing, was included within the treatment system (Figure 14). Flow to all these filtration and coalescence units was

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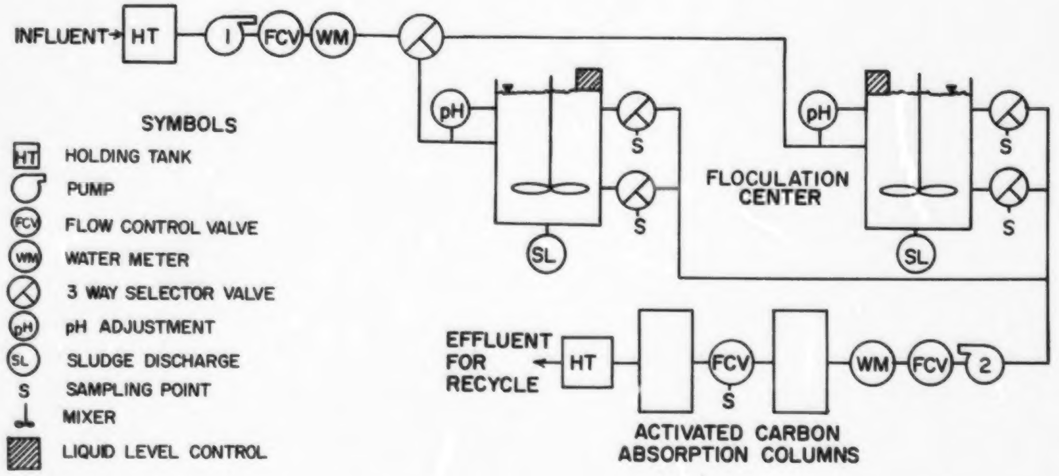
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MIXER
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Figure 10. Schematic diagram of pesticide treatment plant.

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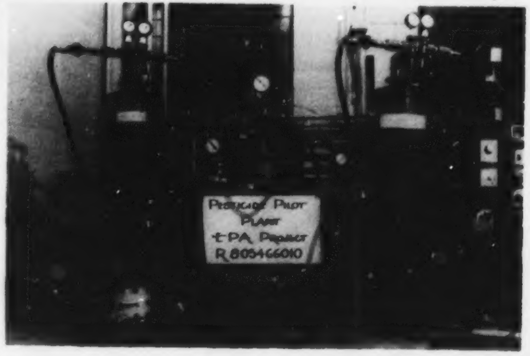
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Figure 11. Pilot plant with mixing tanks, filters, and carbon columns.

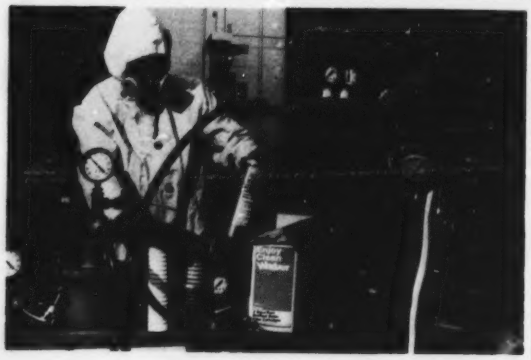

Figure 12. Cuno cartridge filters with 5 and 25 micron filters.

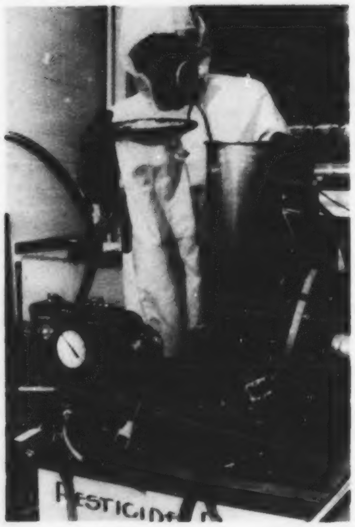

Figure 13. Fabric basket filter with 1 micron screen.

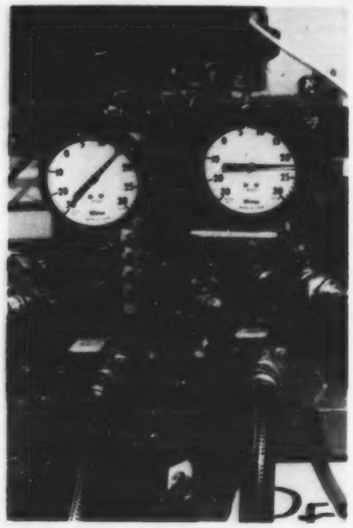

Figure 14. Cartridge coalescers operating at a 10 psi pressure drop.

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measured by a rotameter. Effluent from these units could be directed either to the activated carbon columns or to 378 L (100 gal.) storage tanks to await further treatment.

Two variable speed (0-1800 rpm) mixers were used for chemical mixing and solids flocculation. These mixers were supported on steel frame as shown in Figure 15. for anchoring the mixer. Mounted on this frame was a liquid level control switch to shut-off the pump during filling of the tanks. All electrical controls were centralized on a portable electrical panel that was mounted on one of the frames. The control system is shown in Figure 16.

Each 378 L (100 gal.) tank had three outlets, one approximately .5 m (29 inches) below the top of the tank, the second tap approximately .23 m (9 inches) below the first, and a third tap installed at the apex of the spherical tank bottom. Ball valves were installed at each of these taps.

The mixers were delivered with propeller type mixers. These propellers were adequate for rapid chemical mixing, but the shear forces introduced during batch flocculation hindered the formation of a dense, good settling "floc." A special flat bladed paddle, .3 m (12 inches) long and .15 m (6 inches) high, was constructed and used for both chemical mixing and flocculation.

Two epoxy lined, stainless steel activated carbon columns were used in the pilot plant. The columns had a diameter of approximately .25 m (10 in.) and a height of 1.2 m (4 ft.).

The pumps filtration units and activated carbon columns were mounted on a single frame as shown in Figure 17.

9.1 TREATMENT OF FIELD COLLECTED WASTEWATER

The finished pilot plant consisted of four 378 L (100 gal.) ployolefin tanks, two variable speed Lightning mixers, two Balston coalescers, one Ronnigen-Peter fabric-basket filter, one Cuno filtration unit with variable filter media, and two 5 gpm Jabsco pumps. A variety of pesticide mixtures from two sources were analyzed and used to test the effectiveness of the plant in pesticide removal. The first source of wastewater was a small agricultural airport at Monon, Indiana, where the collection system described in Section 7 was installed. The second source of pesticide waste was the Purdue University O'Neil farm.

The samples that were collected contained a wide variety of different types of materials. The treatment of actual field samples gave an indication of the range of possible problems that would be encountered during field testing of the unit.

The first sample obtained for treatment in the pilot plant contained sevin wettable powder and aircraft wash water. This sample was obtained after a very thorough washing of the aircraft. Approximately 5 gallons of excess solution was left in the aircraft and combined with the equipment wash water.

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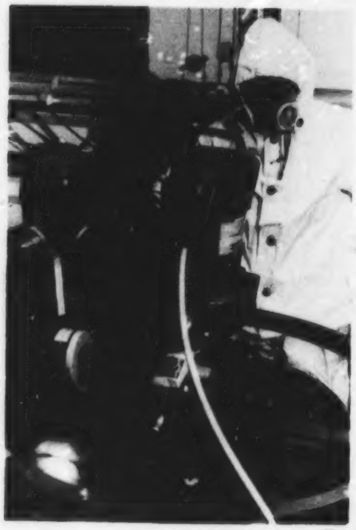


Figure 15. Mixing tanks used for coagulation, flocculation and sedimentation.

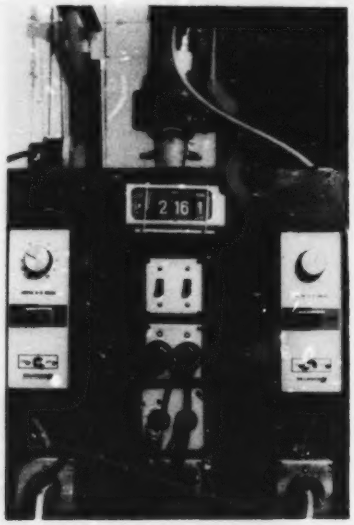
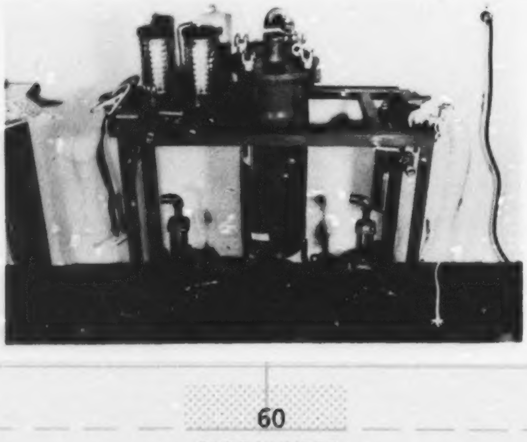


Figure 16. Control panel for mixers and pumps.

Figure 17. Frame for filters and pumps in the pilot plant.



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Initial jar tests were conducted to determine the settling behavior of the wastewater. The initial characteristics of the sample were: pH 7.7, COD 50,000 mg/L, alkalinity 360 mg/L as $CaCO_3$ and suspended solids of 33,000 mg/L. Initially, the wastewater settling characteristics without chemical addition was studied. Although some settling occurred, the high suspended solids concentrations indicated that some form of coagulant addition or filtration would be necessary to achieve efficient solids separation. Separation of solids by filtration through Whatman filter paper reduced the COD from 50,000 mg/L to 810 mg/L.

As a consequence, a large number of jar tests were performed in order to determine coagulants and dosages that would be successful in clarifying this material. Alum was used as the coagulant due to its availability and ease of handling. Possible problems may occur because of the relatively narrow pH range in which alum is effective (pH 6.5-8.0). However, only one solution tested fell outside this pH range, and the pH is easily adjusted to acceptable range.

Excellent removal of suspended solids was achieved with an alum dose of 350 mg/L and a settling time of 45 minutes to one hour. Higher dosages of alum produced only slightly better solids removal. In order to achieve this marginally improved removal, additional alkalinity had to be added to the solution (in the form of NaOH) to insure sufficient alkalinity for complete aluminum ion reaction (1 mg/L of alum reacts with approximately .85 mg/L of alkalinity). The results of one such alum coagulation study are listed in Table 19. Samples were taken from the 2 L beakers at the 1 L depth.

Table 19. Effect of Alum as a Coagulant for Cerberyl Removal

Alum dose (mg/L)	Settling time (min)	Suspended solids (mg/L)
250	30	124
	60	78
300	30	260
	60	96
350	30	56
	60	44
400	30	52
	60	40
450	30	50
	60	40

Further studies were carried out on a wastewater sample collected during construction of the collection system. Wastewater was drawn directly from the gravel drainage area surrounding the concrete pad. The highly colored, turbid wastewater was within a few inches of the gravel surface, and illustrated the inadequacy of gravel infiltration ditches as a means of waste pesticide disposal. This material was identified as sump water, and its characteristics were

COD of 4100 mg/L and suspended solids of 1100 mg/L. No attempt was made to determine the actual pesticides present.

Because alum coagulation was so successful in bench-scale jar testing, full scale tests, that is 378 L (100 gal.) batch experiments, were begun on the carbaryl solution and sump water. Full scale treatment consisted of a chemical addition followed by two minutes of rapid mixing, and approximately 20 minutes of slow flocculation at about 30 rpm, after which time the material was allowed to settle without agitation. Table 20 presents typical results with an alum dose of 350 mg/L for carbaryl wastewater and 375 mg/L for the sump wastewater.

Table 20. Full Scale Treatment of Carbaryl and Sump Water Using Alum as a Coagulant

Settling Time (min)	Sample Tap*	Suspended Solids (mg/L)
	Carbaryl contaminated wastewater	
30	Top	205
	Bottom	225
45	Top	25
	Bottom	52
60	Top	16
	Bottom	42
	Sump wastewater	
30	Top	28
	Bottom	22
60	Top	---
	Bottom	6
Overnight (14 hrs)	Top	---
	Bottom	2

Flocculation and sedimentation, although a relatively simple and effective treatment, could present some problems to pesticide applicators in determining optimum chemical dosages and purchasing the chemicals. For these reasons, filtration of pesticide wastewaters was evaluated. Three different types of filters were analyzed. The first was a disposal cartridge type filter with 25 µ and 5 µ pore sizes. The second filter consisted of a 1 µ pore size fabric mesh supported by a porous metallic basket enclosed in a stainless steel housing. The third filter was a coalescer which consists of fiberglass tubes inserted within a clear plastic housing.

The 25 micron Cuno filter was tested first. The influent to the filter was a carbaryl solution with a suspended solids concentration of 1182 mg/L. A rapidly increase in the pressure drop across the filter was observed with littler reduction in suspended solids. The pressure drop increased from 41 to 104 Kpa (6 to 15 psi) in 15 minutes. The suspended solids concentration of the effluent from the filters was over 1000 mg/L.

The 25 µ filter was also used to treat a dilute solution of alum coagulated sump wastewater with a suspended solids concentration of 32 mg/L. The suspended solids concentration was reduced to 29 mg/L during filtration.

A 5 µ filter was then used on the same supernatant, but at two different flow rates. Again a slight decrease in suspended solids concentration from 29 to 25 mg/L was noted.

Further tests on the applicability of the 5 µ filters were performed on different material. This sample was collected at the Monon airport and primarily consisted of the herbicide paraquat. Sample characteristics were COD 4400 mg/L and suspended solids of 1490 mg/L. The material underwent a significant drop in suspended solids on passage through the filter, along with a sizeable decrease in COD, but the filter was almost immediately blinded, suffering a pressure drop of over 20 psi after operating less than one minute at a flow of one gpm. The effluent had a suspended solids concentration of 25 mg/L and a COD of 1400 mg/L.

Since rapid "binding" was experienced with filters of a larger pore size, the fabric-basket filter was only used with solutions that had been previously coagulated. The treated sump water had a suspended solids concentration of 50 mg/L. The 1 µ fabric basket filter reduced the concentration to 46 mg/L. These results appear surprising in light of the 1 µ pore size of the filter. Three possible explanations of this phenomenon are possible: (1) Either there was an imperfection in the filter media, such as a puncture or weak seam, (2) the non-coagulated particles were less than 1 micron in size (highly unlikely), or (3) the particles were broken up during passage through the filter. Because some leakage around the seam of this unit was observed, the first hypothesis appears the most likely.

The coalescers were considered next. These units were plagued with operational problems from the beginning, most notably leakage around the tubes during high pressure operation. Even though some filtration occurred, since there was a thick layer of solids on the inside of the filter, and the pressure drop reached 270 KPa (40 psi) after treatment of 150 gallons, the leakage around the coalescer tubes precluded the collection of any valid data. Consequently, these units were dismissed from further consideration.

The next step was to evaluate flocculation/sedimentation. Actual field operations would require repeated flocculation-sedimentation in the same tank, with the settled solids building up slowly as each supernatant was drawn off. Therefore, the effect of resuspending and settling the settled solids on solids removal was evaluated. Studies were conducted at both the full-scale and jar-test level. An alum addition of only 50 to 100 mg/L was found to be sufficient to promote good re-settling, as illustrated in Table 21 where alum dosage was 100 mg/L. Alkalinity was added in each case to insure complete reaction of the added aluminum.

Table 21. Flocculation/coagulation/sedimentation for removal of solids using resuspended sludge

Settling time (min)	Sample Tap	Solution Type	Suspended solids (mg/L)
15	Top	Carbaryl	134
	Bottom	Carbaryl	2042
30	Top	Carbaryl	16
	Bottom	Carbaryl	142
45	Top	Carbaryl	6
	Bottom	Carbaryl	10
30	Top	Sump Water	4
	Bottom	Sump Water	2496
45	Top	Sump Water	0
	Bottom	Sump Water	3134
60	Top	Sump Water	0
	Bottom	Sump Water	454

Three coagulant aids, anionic polymer Purifloc A-23 and cationic polymer C-31, both manufactured by Dow Chemical and an anionic polymer 1255 from Watcon were then tested to determine if greater solid removal could be achieved. Both Dow compounds were powders that were difficult to dissolve in water while the Watcon product was a liquid anionic polymer. The pesticide contaminated wastewater from the Purdue O'Neil Farm was treated with 100 mg/L of alum and 1 mg/L of anionic polymer. This treatment was sufficient to reduce the suspended solids concentration from 230 mg/L to 5-20 mg/L in approximately 30 minutes of settling. The degree of pesticide removal achieved by flocculation/sedimentation is summarized in Table 22.

Table 22. Pesticide Removal by Pilot Plant Using Alm and Anionic Polymer

Treatment	Removal of Indicated Pesticide in Percent Monitor	Lannate	Carbaryl
Settled 3 days w/o chemicals	---	90%	50%
Alum addition - settling time 30 min.	19%	82%	43%
Alum + polymer addition settling time 30 min.	64%	89%	56%

Another sample was collected from Monon that contained a wide variety of compounds. This wastewater was jar tested and then treated full-scale by adding 100 mg/L $FeCl_3$ (roughly equivalent to 50 mg/L of alum) and 1 mg/L of anionic polymer. No significant improvement in supernatant quality was seen when dosages as high as 400 mg/L $FeCl_3$, were applied as long as 1 mg/L of anionic polymer is provided. It was observed, as expected, that when the new solution was mixed with settled solids removed from previous treatments, a clearer dividing line between solids and supernatant was seen, along with a slightly faster settling rate.

At this point, all the settled solids from previous treatments were combined into a single tank. The purpose of this test was to determine the settleability of previously flocculated and settled solids. When this solution was mixed, a thick suspension was obtained with a suspended solids concentration of about 17000 mg/L. When 1 mg/L of anionic polymer was combined with 100 mg/L of alum, a supernatant with excellent clarity was produced.

The next sample of pesticide contaminated wastewater from the Purdue O'Neil farm presented some serious problems. The methods of coagulation that had been used were completely unsatisfactory. To solve this problem several techniques were evaluated. Acid cracking of the emulsion with varying dosages of sulfuric acid was unsuccessful. The problem was that 300 mg/L of a wetting agent had been added to coat the leaves of cabbage plants with the insecticide. Review of industrial waste treatment literature indicated that calcium precipitation of wetting agents has been used with success. For this particular sample, which had a pH of 5.85, the pH was raised to 10 with lime $(CaOH_2)$, yielding a calcium to surfactant ratio of approximately 2:1 on a molar basis. Rather than drop the pH down to an acceptable range for subsequent alum addition ferric chloride was used as the coagulant. Dosages of about 600-800 mg/L of ferric chloride with anionic polymer were needed to achieve good clarity in the supernatant during jar tests. However, when the material was diluted to a concentration similar to equipment wash water it was only necessary to raise the pH to 9.5 with lime addition and to add 200 mg/L of ferric chloride and 1 mg/L of anionic polymer to achieve good clarity.

At this point, a technique that had been studied in the Environmental Engineering Department of Purdue University to clarifying thick suspensions of clay material was tested. This procedure involved addition of a powdered activated carbon (PAC) and a cationic polymer. The addition of calcium hydroxide and about 5 g/L of PAC, 1 mg/L of cationic polymer alone was sufficient to clarify the material. Due to the "messy" nature of working with powdered activated carbon and the added expense of using PAC on a full scale basis this method was not compared to an activated carbon adsorption of pesticides.

Treatment of this wastewater demonstrated the need for the addition of calcium salts to clarify surfactant bearing materials. Because many pesticides release highly toxic intermediates upon alkaline hydrolysis, and also to preclude the possibility of raising the pH above the acceptable range for alum addition, calcium chloride is now being used in preference to lime.

The next batch of wastewater collected at the Monon airport contained paraquat. The original characteristics of the waste were COD 4400 mg/L, suspended solids 1490 mg/L and pH 7.58. The wastewater was mixed with previously settled solids, 100 mg/L of alum and 1 mg/L anionic polymer. The results are presented in Table 23. The large reduction in suspended solids would indicate that this wastewater is amenable to the flocculation/sedimentation treatment.

Table 23. Flocculation/coagulation/sedimentation as a means of a paraquat removal

Settling Time	Sample Tap	COD (mg/L)	Suspended Solids (mg/L)
45 minutes	Top	3,650	295
	Bottom	55,000	24,360
90 minutes	Top	2,975	36
	Bottom		

Previous tests indicated that increased concentrations of solids can lead to better settling behavior and decreased polymer dosages. Therefore, the settling rates of a tank that contained a bottom solids concentration of 95,000 mg/L with a solids layer of approximately .50m (20 in.) was determined. When the solids were suspended the concentration was approximately 20,000 mg/L. The second tank had a resuspended solids concentration of 7500 mg/L. Resuspension took place by mixing with the wastewater from the Monon airport. The first tank was first treated solely with 1 mg/L of anionic polymer, and it took approximately 90 minutes for the solid-liquid interface to fall below the bottom tap. Supernatant suspended solids were 36 mg/L. A replicate of this test, but with 100 mg/L alum added as well, gave essentially the same results, indicating that coagulant addition provides no measurable improvement when highly concentrated solutions are involved. The supernatant COD was 2400 mg/L.

The final sample collected at Monon had a COD of only 600 mg/L and suspended solids of 172 mg/L. Jar test treatment showed that conventional alum and polymer treatment did not produce a good quality supernatant. However, addition of .5 to 1 gm/L of calcium, introduced as calcium chloride, allowed for good clarification. This indicated the presence of some surfactant material which was further evidenced by the formation of a surface foam upon mixing. Where jar testing is not possible before treatment, calcium addition as a matter of course would perhaps be desirable.

Next activated carbon adsorption of pesticides was evaluated. Table 24 illustrates carbon adsorption of the carbaryl in wastewater. The wastewater was passed through the carbon columns twice. The first pass, at approximately 11 L/m (3 gpm) (4.2 L/s-m^2) did not achieve acceptable effluent quality, so a second pass at 3.8 L/m (1 gpm) was made. This flow rate of 3.8 L/m has been maintained for all further studies and gives an approximate contact ime of 8 minutes in each bed. The two columns were used in series, with the first column containing approximately 37 Kg (80 lbs.) of Filtrasorb 300 (Calgon Corporation) while the second contained an approximately equal amount of Nuchar WV-G (Westavco Chemical Division). Samples were first contacted with the Filtrasorb. Analysis of carbaryl concentration on both carbon effluents were performed. The Nuchar effluent represented the plant's final effluent. Obviously, slowing down the flow rate made a dramatic difference in the degree of pesticide removal.

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Table 24. Carbaryl removal by absorption on activated carbon columns (influent carbaryl concentration 475 mg/L).

Sample	Carbaryl (mg/L)
First pass - 3 gpm	
Filtrasorb effluent	
75 gallons	48
100 gallons	26
125 gallons	21
150 gallons	20
Nuchar effluent (final product)	
35 gallons	16
65 gallons	10
100 gallons	28
125 gallons	11
150 gallons	6
Second Pass - 1 gpm	
Filtrasorb effluent	
50 gallons	<1
Nuchar effluent	
25 gallons	<1
50 gallons	<1

Carbon studies were also run on the sump water after coagulation and sedimentation. The results are summarized in Table 25. Since the wastewater contained several different compounds the results are expressed as percent removals based on the reduction in peak height using gas chromatographic analysis.

In most cases 90 percent or better pesticide removal was obtained from second (Nuchar) column.

Table 25. Activated carbon columns for removal of pesticides from sump water

Sample	Removal of Indicated Peak (percent of influent) 1	2	3	4
Filtrasorb effluent				
100 gallons	79.0	81.2	89.4	91
150 gallons	90.2	88.2	92	91
175 gallons	67	83	90	97
200 gallons	58.7	78	87	89
225 gallons	58	76	87.9	96
250 gallons	79.5	89.9	93.8	97
275 gallons	45	66.8	77.7	91
Nuchar effluent				
25 gallons	74.2	87.2	93.7	79
30 gallons	94.5	93.5	97.5	88
100 gallons	98.0	91.5	96.4	—
125 gallons	53.8	63.1	83	—
175 gallons	70	89.5	91	94
200 gallons	79.1	77.8	84	93
225 gallons	94.7	92.6	95.2	97
250 gallons	95	95.6	—	99
275 gallons	49.3	76.9	90.1	96

9.2 TREATMENT OF MALATHION CONTAMINATED WASTEWATER

Malathion contaminated wastewater was also used to evaluate the treatment process. These studies were limited to synthetic solutions only, that is, malathion, as an emulsifiable concentrate, was added to either tap water or previously collected aircraft wash water samples, to test the process on emulsified formulations.

9.2.1 Flocculation/Sedimentation Treatment of Malathion

As a first step, sedimentation without chemical addition was evaluated. A 45 percent malathion emulsifiable concentrate was added to 378 L (100 gal.) of pesticide solution with associated solids from re-suspension of pre-settled alum floc to give a malathion concentration of 180 mg/L. A supernatant containing only 90 mg/L was obtained after approximately 1 hr. of sedimentation. Allowing the material to settle overnight did not yield any significantly greater reductions in malathion concentration. Apparently, settling of the suspended solids present from previous alum flocculation provided a filtering action so that the emulsion droplets were carried down along with the floc. The supernatant was quite turbid, indicating that more complete solids removal could be accomplished by adding a coagulant.

To test the efficiency of flocculation/coagulation/sedimentation on emulsified malathion, a series of jar tests were set-up. Initial tests were performed on a solution of malathion and tap water. As with previous jar tests, commercially available alum, sufficient alkalinity, and Dow Anionic Polymer A-23 were used. Malathion concentration was 180 to 200 mg/L. Table 26 shows the results for the first series of jar tests.

Table 26. Jar test results for malathion

Chemical dose Alum mg/L	 Polymer mg/L	Final Malathion Concentration mg/L
0	0	90
50	1	69
100	1	39
200	1	41
400	1	41

Several observations can be made from these tests. Alum dosages of 100 mg/L or greater appear to give a maximum pesticide removal. The presence of floating solids for the highest dosages of alum may be an artifact of hindered settling behavior within the small volume jars (2 liter beakers). At this dilute malathion concentration, polymer alone is insufficient.

The order and timing of chemical addition to the pesticide solution was found to affect the resulting supernatant quality. In particular, polymer addition was found to be ineffective unless added as the final step. The optimum chemical addition was found to be as follows. However,

1. Add alum; allow 30 seconds for mixing
2. Add hydroxide (or other source of alkalinity), allow one minute for mixing
3. Add polymer, and allow 45 seconds for mixing
4. Flocculate material for approximately 10 minutes at 30 rpm.

Jar testing of wastewater samples were then performed to determine the effect of initial suspended solids concentration. Table 27 shows typical results. Initial malathion concentration was 180-200 mg/L.

Table 27. Jar test evaluating the effect of solids concentration on malathion removal

Chemical dose		Malathion concentration		
Alum mg/L	Polymer mg/L	Initial mg/L	Final mg/L	Suspended solid mg/L
100	1	200	21	24000
300	1	200	26	24000
0	1	200	81	24000
100	1	200	28	2400
300	1	200	19	2400
0	1	200	75	2400

The conclusion drawn from these studies was that the solids concentration had little effect on emulsion removal. The higher suspended solids concentration did remain turbid after flocculation. By diluting the wastewater to a suspended solids concentration of approximately 12,000 to 15,000 mg/L a clear supernatant could be produced by alum coagulation, polymer addition and sedimentation. Concentrations above this point gave murky solutions even at high coagulant dosages. All further jar test evaluations were done on solutions whose suspended solids had been adjusted to between 12000 and 15000 mg/L.

The concentration of malathion was also varied. A series of tests yielded the data shown in Table 28. All solutions had a suspended solids of 12,000 mg/L, with 200 mg/L alum and 1 mg/L A-23 polymer added to each.

Table 28. Jar test evaluation of flocculation/sedimentation to remove various concentrations of malathion.

	Malathion Concentration	
Jar	Initial mg/L	Final mg/L
1	10	9-14
2	30	9-11
3	75	11-13
4	150	15-18
5	300	20-25

By adjusting the suspended solids concentration to 1200 mg/L supernatant quality was improved. Reductions of malathion concentration to 25 mg/L or less are consistently achievable when good supernatant clarity is obtained. As in all other cases, final sludge volume was approximately 25 percent of the original solution volume after 30 to 45 minutes of settling.

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A number of additional coagulant polymers were also evaluated. WATCON Inc. provided three chemicals: a liquid anionic polymer, a cationic polymer and a nonionic polymer. For the removal of solids, the anionic was again found to be the most effective, although for emulsion removal both the cationic and anionic appeared to be equally effective. The anionic was used for further testing because of its broad applicabilty to all formulation types. Optimum liquid polymer dosage was found to be approximately

A final set of jar tests for malathion removal was conducted to test any effects of varying alum dosages while adding .4 mL/L WATCON Anionic polymer. The results shown in Table 29 were obtained when field collected pesticide solutions were mixed with pre-settled solids, diluted to approximately 12,000 mg/L, and "spiked" with malathion and then treated with various doses of alum. Effluent quality was dependent on the initial malathion dosage, and was essentially independent of coagulant dose.

Table 29. Jar test evaluation of alum dosage on malathion removal

Alum dose mg/L	Malathion initial mg/L	Concentration final mg/L
200	20	10-16
500	20	10-13
200	200	43-58
500	200	42-56
200	500	43-61
500	500	38-51

9.2.2 Full Scale Flocculation/Coagulation/Sedimentation Studies of Malathion

During full-scale testing of the flocculation procedure, 1 to 1.5 hrs. were required for complete settling. When a sample with an initial suspended solids concentration of 24000 mg/L was spiked with 200 mg/L malathion and treated the supernatant contained only 35 mg/L malathion. Studies with spiked tap water showed a supernatant concentration of 55 mg/L. These results confirmed jar test results. Identical tests were later performed with more dilute solutions. Even though one of these pesticide solutions was spiked with as much as 400 mg/L of malathion, supernatant levels were measured at 41 mg/L malathion after 1 hr. of settling. Increased alum dosages did not produce significantly better pesticide removal from tap water solutions, as 500 mg/L of alum reduced a 200 mg/L malathion solution down to 30 mg/L. As the solids built up after repeated coagulation and sedimentation, the clarity of the supernatant decreased. Concentrations of malathion as high as 84 mg/L were observed. However, dilution of this material to between 12,000 to 15,000 mg/L suspended solids, spiking with 200 mg/L of malathion and coagulation with 200 mg/L alum, produced a supernatant malathion concentration of 27 mg/L. No change in this value was observed after 18 hrs. of settling.

9.2.3 Carbon Studies

Full-scale carbon column studies were conducted by pumping 1500 L (400 gal.) of this treated malathion contaminated wastewater through the two columns. No malathion was detected in the effluent. Since about 15000 L (4000 gallons) of wastewater would have to be treated to exhaust the full-scale columns the carbon exhaustion studies were performed on two laboratory columns. The columns were 2.54 cm (1 inch) inside diameter and held 25 grams of activated carbon. The carbon was first washed with distilled water to remove "fines" then dried overnight at 103 C before weighing. The feed solution of malathion was continuously fed to the column by means of a constant head tank arrangement and effluent samples were taken at convenient intervals. Each column was equipped with fine mesh screens in the inlet and outlet to prevent carbon loss. Approximately 10 to 12.5 cm (4 to 5 inches) of glass beads of graduated size were placed at the inlets to provide for flow distribution. The columns were run in the up-flow mode.

Malathion solutions were made up by adding 100 mg/L of emulsifiable concentrate malathion to distilled water. The solution was allowed to settle for approximately 12 hrs., and a sample was refrigerated for later analysis. The remainder of the solution was fed to the column. Near the end of each batch of pesticide, a second sample was taken for analysis to determine any changes in concentration. The pH was adjusted to prevent hydrolysis. The concentrations of solutions fed to columns were between 59 and 64 mg/L.

A summary of results can be found in Table 30 and the exhaustion curves are plotted in Figure 18. Ultimate capacity was found to be quite close for the Filtrasorb and Nuchar adsorbents. The adsorption capacity of Filtrasorb at a 3 mg/L breakthrough concentration was computed to be 17.1 percent by weight while that of Nuchar was found to be 18.8 percent. Exhaustion capacity where influent and effluent concentrations are equal, was determined as 28.4 percent by weight for Filtrasorb and 27.3 percent for Nuchar.

9.3 TREATMENT OF METRIBUZIN CONTAMINATED WASTEWATER

Since triazine herbicides are heavily used throughout Indiana and the Midwest for the control of broadleaf weeds and annual grasses, tests of the efficiency of the treatment system in removing metribuzin were initiated.

Metribuzin was chosen for analytical convenience since a distinct peak appears from the gas chromatograph using an electron capture detector. The molecular structure of this herbicide is similar to the other triazines, but the capacities of the system would be severely tested because of the high water solubility of metribuzin (1220 mg/L) as opposed to other triazines, such as atrazine (water solubility of 33 mg/L) and prometryne (water solubility of 48 mg/L).

It is important to note that synthetic metribuzin solutions differed in one important aspect from the other solutions previously treated. In the case of metribuzin, pure pesticide was used for solution make-up rather than formulations. Whereas previous removals, at least during the

Table 30. Carbon column exhaustion study for malathion

Liter passed through column	Effluent conc (mg/L)	 absorbed (mg)	Total weight conc (mg/L)	 absorbent (mg)
25	0	1500	0	1550
42	0	2520	0	2620
47	0	3500	0	3625
60	2	4030	2	4370
66	3	4280	2	4720
76	3	4630	4	5180
90	5	5130	4	5520
100	12	5490	8	5760
116	17	6060	11	6140
136	45	6680	42	6740
150	45	6890	58	6820
165	62	7110	60	6825

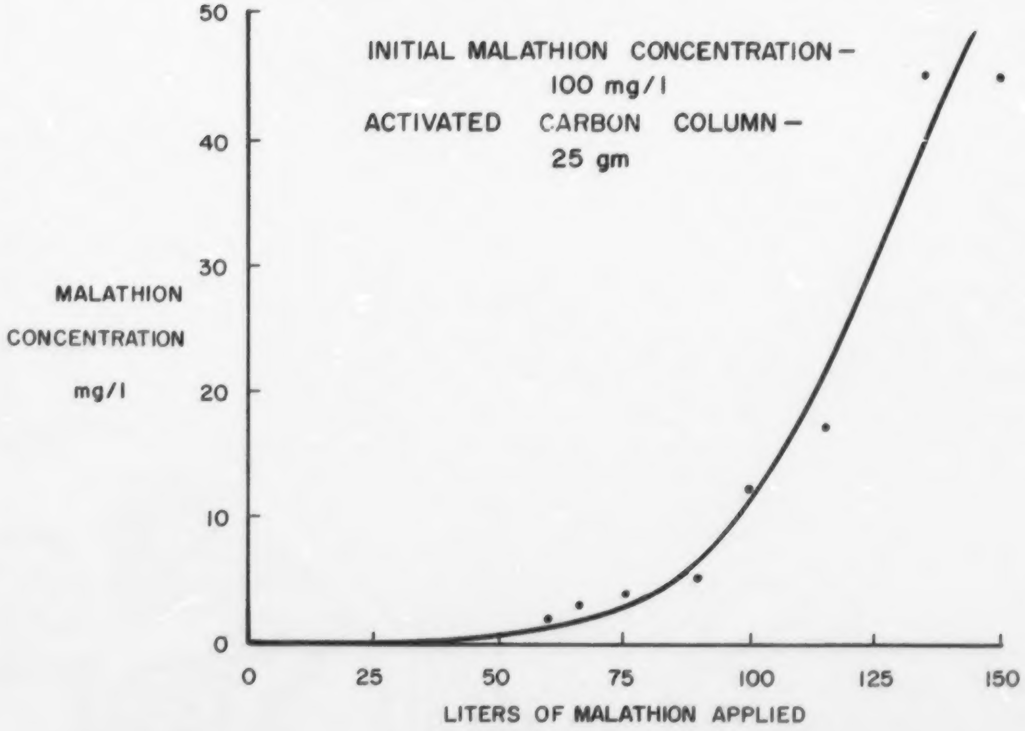

Figure 18. Carbon adsorption of malation in 25 gm column of Filtrasorb 400.

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flocculation/coagulation/sedimentation procedures, were primarily a result of removing wettable powders granules or emulsified droplets, no such behavior could be expected with metribuzin.

Jar test procedures were used on a metribuzin contaminated wastewater. An alum dosage of 200 mg/L with .4 mg/L of WATCON anionic polymer, was used. The results are summarized in Table 31.

These results demonstrated that suspended pesticide, above the water solubility, was removed, while the dissolved material was unaffected.

Table 31. Jar test evaluation for flocculation/sedimentation removal of metribuzin

Metribuzin Concentration Initial (mg/L)	Final (mg/L)
100	100
250	260
750	600-675
2000	1000
2500	1000-1025
4000	1176

The effect of alum dosage on metribuzin removal was evaluated with the next series of jar tests. The results are summarized in Table 32.

Table 32. Effect of alum dosage on metribuzin removal by flocculation/sedimentation

Alum dosage mg/L	Metribuzin Concentration Initial mg/L	Final mg/L
200	93	91
500	93	90
200	310	300
500	310	330
200	930	975
500	930	975
200	1550	1250
500	1550	1125
200	1940	——
500	1940	1068
200	3100	——
500	3100	1000

A repeat of these tests was performed on actual resuspended pesticide wastewater that had been "spiked" with metribuzin. These results, shown in Table 33, are consistent with previous studies. No attempt was made to determine the removals of other components that may have been in the wastewater.

Table 33. Effect of using suspended solids on metribuzin removal by flocculation/sedimentation

alum	Metribuzin Concentrate Initial conc. (mg/L)	Final conc. (mg/L)
200	100	81
500	100	90
200	500	330
500	500	315
200	750	585
500	750	585
200	1250	1050
500	1250	1000-1125
200	2000	996
500	2000	982
200	3000	920
500	3000	1000

Full scale flocculation/coagulation/sedimentation tests were performed to check the validity of applying jar test data to large-scale operations. By mixing resuspended pesticide waste with 200 mg/L of metribuzin, then adding 200 mg/L alum and associated chemicals, the supernatnat metribuzin concentration was reduced to be 115 mg/L. A repeat of this test with 264 mg/L metribuzin produced a supernatant concentration 140 mg/L. The 85 to 120 mg/L of metribuzin that was removed is consistent with the results of the jar test.

The supernatant from these settling tests was then passed through the two activated carbon beds. When the solution was first contacted with Nuchar carbon, the metribuzin level showed an almost immediate breakthrough of 6 mg/L, a value that was steady for the 190 L (50 gals.) of solution treated. No pesticide was found in the effluent from the second column containing Filtrasorb carbon. When the order of carbon contact was reversed, as before, no pesticide was found in the Filtrasorb effluent. As both carbons were relatively fresh, differing response of the carbons were most probably due to differences in relative affinity for this particular herbicide.

As in the case of malathion, capacity determinations for metribuzin adsorption were made on laboratory scale columns. All conditions are the same as those previously described, although the concentration of pesticide was much higher. Influent to the Nuchar carbon contained 980 mg/L while Filtrasorb, due to limitations in the amount of pesticide available, received an influent of 800 mg/L. The data is presented in Table 34.

Table 34. Carbon column exhaustion study for metribuzin

Liters	Nuchar effluent metribuzin conc. (mg/L)	Nuchar weight absorbed (mg)	Filtrasorb effluent metribuzin conc. (mg/L)	Filtrasorb weight absorbed (mg)
2	<1		<1	
	<1	3912	<1	3200
4	5	5864	40	4760
6	220	7600	160	6160
12	430	10,172	183	8680
13	515		216	
14	740	10,648		
15			392	10,000
17	982	10,948	515	11,280
18			737	12,219
20			782	12,256

Nuchar was found to have an overall capacity of 43.8 percent while Filtrasorb showed a slightly better value of 48.8 percent.

It should be noted that the computed capacity of the carbons do not necessarily reflect the adsorption capacity to be expected during actual field operations. Although using carbon columns in a series operation would allow realization of high capacities, that is, the first column in the series could be driven to exhaustion while later columns could be used to "scrub" the effluent, influent concentration and the presence of other pesticides can affect the adsorption efficiency of a carbon type for a particular pesticide.

SECTION 10

SYSTEM ECONOMICS

Implementation of a system to handle the disposal of the wash and rinse water from pesticide applicators would require a coordinated approach by regulatory agencies. Since commercial pesticide applicators are registered and are required to recertify periodically by attending educational programs, it is relatively simple to instruct pesticide applicators on the availability of a treatment and disposal system. Implementing the treatment system for all commercial applicators may be more difficult. Four alternative techniques were proposed. The four possible treatment schemes are: 1) an on-site treatment plant to handle all waste water from the applicator, 2) several mobile treatment plants to service aerial applicators in a region on a routine basis, 3) a mobile system that would serve all aerial applicators in the entire state of Indiana, and 4) a centralized treatment plant that would receive the wastewater from all ground and aerial applicators in the state. Since aerial applicators appear to have the greatest demand for such a treatment technique, alternatives 1 and 2 were evaluated on the basis of handling only the aerial applicators. Plans 3 and 4 could include additional pesticide applicators in the state.

Practical considerations dictate that the treatment system or storage facilities must be adequate to handle the peak demands of the applicator. During the peak of the season the aircraft may be washed as many as four times a day and operate for 5 days a week. This would require 20 washes per week, giving a total wastewater generation of approximately 1900 L (500 gal.) per week. The seasonal demand by these aerial applicators would be much lower. The operator sprays for only 5 months of the year and because of weather and other constraints, usually only half of these days are suitable for aerial application. The average annual wastewater production was estimated to be two washes per day during the 75 days of operation for a total of 150 washes per season or approximately 4,000 gallons of wastewater. The same volumes of wastewater were assumed for ground applicators.

Of the approximately 2,000 registered applicators in Indiana there are only 46 aerial applicators and only 482 commercial ground applicators that work primarily in agriculture. These registered applicators were located on the state map of Indiana. It was found that the 46 aerial applicators were located in 37 counties. These applicators could be subdivided into six regional areas, with each region serviced by one mobile treatment plant. Table 35 illustrates how these areas could be subdivided.

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Table 35. Distribution of aerial applicators

Counties	No. of Applicators	Max. vol. of waste generated per week (m^3)	Total annual waste water produced (m^3)
Newton, Jasper, White Cass	7	13	106
St. Joseph, Eklhart, LaGrange, Dekalb, Noble, Kosciusko	7	13	106
Wabash, Wells, Howard, Grant, Delaware, Jay, Randolph, Union	9	17	136
Sullivan, Vigo, Parke, Fountain, Montgomery, Tippecanoe	7	13	106
Clinton, Hamilton, Hancock, Hendricks, Marion, Shelby, Decatur	9	17	136
Jackson, Jefferson Harrison,, Gibson, Posey, Vanderburgh, Warrick	7	13	106
TOTAL	46	86	696

If all agricultural related applicators in the state of Indiana were included the total number of applicators would be increased by 482 to a total of 528. The total amount of waste generated in one year would then be about 7560 L (2 x 10^6 gallons).

10.1 PLAN 1 — INDIVIDUAL TREATMENT PLANTS

Because aerial applicators are already trained in handling pesticides and, concurrently, operate a high technology application system, it would seem reasonable to expect that these applicators would be capable of managing a waste treatment facility to treat the pesticide contaminated wash and rinse water from their equipment. Numerous applicators appear to be interested in constructing the type of system used at Garwood Airport in Monon, IN and are quite willng to take the responsibility of training an individual to manage the system. Since our proposed treatment plant is a fairly low technology operation, it should pose no great operating difficulties. However, a few safety features should be included in such a system as discussed in Section 5. The treatment system would be composed of two flocculation/sedimentation tanks and three activated carbon columns. The applicator would send a sample of the wastewater through the first carbon column to a laboratory each month. The two additional columns would be used to insure a clean effluent so that the spent carbon column would be removed before pesticides were discharged to the environment. Table 36 illustrates the cost of such a system. It is estimated that the annual cost to the applicator would be about $6000/year.

The main advantage of this type of treatment system would be that the aerial applicators could operate the plant when they had an adequate volume of wastewater. A 1900 L (500 gal.) tank would be used to store the pesticides until an adequate volume to justify the operation of the treatment plant had accumulated. Treatment could be done once a week during heavy application schedule and less frequently during the rest of the year. Another advantage in such a system would be the increased chance of acceptance by the applicator. Most aerial applicators want to manage the system on their own site. The major disadvantage of such a treatment system would be the inability of the local applicator to handle severe problems. Based on this research, the additions of caustic, alum, calcium salt and organic polymer has successfully coagulated all types of pesticide wastewaters. Activated carbon acts as a safeguard to insure the removal of water soluble and unsettled materials through both adsorption and filtration mechanisms. The applicator would have to be responsible for proper disposal of the sludge and carbon. Once-a-year collection of the spent activated carbon and sludge by a commercial disposal firm could alleviate this problem.

Table 36. Economics of installing and operating a treatment plant for each applicator

	Individual	State Wide
Capital Cost		
Utility Building	1000	46000
Treatment Plant		
Tanks	400	
Pumps	400	
Mixer	900	
Columns	1200	
Contingency	600	
Treatment Plant Subtotal	3500	161000
Collection system	2000	92000
Total Capital Cost	6500	299000
Annual Cost		
Depreciate, interest, repairs taxes, and insurance	1650	
Salaries and labor	350	
Chemicals	200	
Disposal of Sludge and Carbon	2500	
Lab analysis	300	
Contingency	750	
Total annual cost	57500	264500
Annual cost per applicator	5750	

10.2 PLAN 2 — SIX MOBILE TREATMENT STATIONS SERVING 7-9 AERIAL APPLICATORS

The second alternative that should be considered in the implementation of a statewide system is the use of mobile treatment systems to service various regions. The mobile treatment plants could be transported to a particular applicator site on a truck or trailer. If the system was sized to handle 7 to 9 applicators in a two-week period, the capacity would have to be at least .25 L/s (4 g/min.). This calculation is based on the assumption that each applicator would have a 3780 L (1000 gal.) storage tank for collection of the wastewater and that the entire tank volume and would have to be treated in 5 hours. This scheme would presumably allow sufficient time for round trip travel to the site and complete wastewater treatment within a single day. The treated wastewater would be returned to the applicator for possible re-use. describes the cost of such a treatment system. The applicators could be expected to pay approximately $7000 per year.

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The major advantage of this type of treatment plan would be that an experienced individual could be hired to operate the treatment plant. The treatment plant could also be used in a southern state during the winter and returned to the midwest during the summer. Year-round use of the system would reduce the cost. The second advantage of this system is that since the treatment plant would come to the site every 2 weeks the potential problems arising in the treatment of highly mixed pesticide wastes could be minimized.

The major disadvantage of this type of system is the additional cost of having six mobile stations. In addition, the periodic nature of the wastewater generation could possibly create a difficulty in managing the routing of these mobile stations. It would also be more difficult for the treated wastewater to be reused by the applicator for dilution of additional pesticide samples, as an additional storage tank would have to be installed for storing water that was returned to the applicator after the wastewater had been treated.

Table 37. Economic evaluation of a regional mobile treatment plant

	Mobil Unit	State Wide
Capital Cost		
Truck & Trailer	35000	210000
Treatment Plant		
Tanks	1200	
Pumps	600	
Mixer	1000	
Columns - 2000	3000	
Construction	1000	
Contingency	1000	
Treatment Plant Subtotal	7800	46800
Collection System	16100	105800
Total Capital Cost	58900	362600
Annual Cost		
Depreciation, interest, repair taxes and insurance	15000	91000
Salaries	15000	90000
Chemicals	1000	6000
Disposal	10000	60000
Lab analysis	2250	10000
Transportation	1250	7500
Contingency	7000	42000
Total Annual Cost	51500	307500
Annual Cost Per Applicator	7400	6700

10.3 PLAN 3 — ONE MOBILE TREATMENT SYSTEM TO SERVE THE 46 AERIAL APPLICATORS

If the size of the mobile treatment system was increased it would be possible to handle all aerial applicators Indiana on a once-a-year basis. The individual applicators would have to have the capacity to store at least 5,000 gallons of wastewater. The treatment facility would have to be capable of treating and processing the wastewater in a 1-day period, necessitating a flow rate of approximately .7 L/s (11 gal/min). Table 38 describes the cost of such a treatment facility. These costs are divided into two categories. The first column shows the cost if only aerial applicators are involved. Each applicator would have to pay $4000 per year. If the system were used to treat a total of 150 applicators the cost would be reduced to $2500 per year.

The major advantage of this treatment alternative would be the capability of hiring a highly trained operator and of providing some analytical capabilities on the treatment unit. Again, as in Plan 2, a large tank would have to be installed at each site to store both wastewater and treated water, if it were to be reused.

The major drawbacks of such a system would be the lack of backup equipment if any problem occurred with the mobile treatment truck. A small mechanical failure could cause delays in the servicing of the sites. Furthermore, routing to achieve maximum efficiency of the vehicle would be difficult.

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Table 38. Economic evaluation of state wide mobile treatment plant

	Aerial Applications	150 pesticides applications
Capital Cost		
Truck and Trailer	50000	50000
Treatment Plant		
Tanks	2000	
Pumps	3000	
Mixer	1800	
Columns	6000	
Construction	5000	
Contingency	2700	
Treatment Plant Sub Total	20500	20500
Collection system	115000	375000
Total Capital Cost	185500	445500
Annual Cost		
Depreciation, interest, repairs taxes, insurance	56000	111000
Salaries	60000	90000
Chemicals	6000	18000
Disposal	20000	60000
Lab Analysis	10000	30000
Transportation	7500	22500
Contingency	22400	50000
Total Annual Cost	171900	381500
Annual cost per applicator	3800	2500

10.4 PLAN 4 — CENTRALIZED TREATMENT FACILITY

The last alternative to consider would be the construction of a central treatment plant. This alternative might be attractive if all pesticide applicators in the state were required to treat their wastewater. The capacity of the treatment works would have to be at least 2 L/s (35 gal/min.) if all pesticide applicators were involved. Each applicator in Indiana would install a 1900 L (5,000 gal.) storage tank which would be emptied once each year by a tank truck. By operating three tank trucks it would be possible to wait until the tanks at the individual sites were full thus enabling the individual applicators could call for pick-up and subsequent treatment. The proposed budget for such a system is shown in Table 39. If only aerial applicators are involved the cost of the service would be about $5000 per year. With all applications involved the cost would be $2000 per year.

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The major advantage of this treatment alternative would be the reduced cost per applicator. The major disadvantage of such a system would be the inability to return the water to the applicator. This effluent would have to be discharged to a publicly owned waste treatment plant or possibly used as irrigation water near the treatment plant. Furthermore, public acceptance of such a facility may be difficult to obtain, with associated problems with public relations and land availability.

Table 39. Economic evaluation of a central treatment plant

	Aerial Applicators	All Applicators
Capital Costs		
Trucks	50000	150000
Land	10000	15000
Building	75000	100000
Treatment Plant		
Tanks		
Influent	10000	20000
effluent	10000	10000
flocculation/sedimentation	2000	4000
Pumps	3000	4000
Mixers	3600	5400
Columns	6000	18000
Construction	15000	25000
Contingency	7500	13000
Treatment Plant Subtotal	57100	99400
Collection System	115000	1320000
Total Capital Cost	307100	1684400
Annual Cost		
Depreciation, interest, repairs taxes and insurance	77000	421000
Salaries	90000	140000
Chemicals	5000	50000
Disposal	20000	200000
Lab analysis	5000	50000
Transporation	7500	75000
Electricity	1200	2400
Contingency	30000	134000
Total Annual Cost	231200	1027400
Annual cost per applicator	5026	2000

10.5 SUMMARY OF TREATMENT OPTIONS

The four systems are summarized in Table 40. Based on the reaction of most pesticide applicators a simplified version of option 1 with individual treatment plants is most likely to be accepted. Appendix 1 describes how such a simplified system might be installed.

Table 40. Summary of Alternative Systems for Treatment of Wastewater from Pesticide Applicators

	Plan 1 Individual Plants	Plan 2 Six Mobile	Plan 3 On Mobile		Plan 4 Central	
			Aerial Only	150 Applicators	Aerial Only	All Applicators
Investment						
collection	2000	2300	2500	2500	2500	2500
treatment	4500	43800	70500	70500	192100	364400
Annual Cost	5750	6700	3800	2500	5000	2000
Transport of wastewater	no	no	no	no	yes	yes
Transport of sludge	annually	yes	yes	yes	annually	annually
Train applicator	yes	no	no	no	no	no
Energy consumption	low	medium	medium	medium	high	high
Reuse of effluent	easy	possible	possible	possible	no	no
Potential for discharge	high	med.	high	medium	medium	low
Expertise of operator	low	med. low	medium	medium	high	high

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APPENDIX

Numerous pesticide applicators have requested information on how to treat the wastewater produced during cleanup of equipment. Through the financial support of the U.S. Environmental Protection Agency and the North Central Regional Pesticide Impact Assessment Program we were able to develop a system that would remove pesticides from wastewater. This system was quite simple and we believe it to be applicable to many small applicators. The procedure outlined has been used on about 30 different classes of insecticides and herbicides and so far no serious problems have appeared. There are numerous other possible mixtures which may present more severe questions. It is normally very simple to observe when the system is malfunctioning. The effluent from the carbon columns should be odorless and colorless. If either odor or color are present you should contact us for advice.

The procedures described in the bulletin can be used by a small scale applicator that would only need to treat 50 gallons of wastewater at a time. The treatment plant can be enlarged to handle larger volumes. The same recipe can be followed with proportional increases in each ingredient.

With regard to the manufacturers and suppliers mentioned as sources of equipment, chemicals and supplies, no endorsement is being made. Any other source of equipment would be acceptable. The list is included only as a guide to you in obtaining the necessary equipment.

A. Procedure for Treating Pesticide Contaminated Wastewater (See Figure 19)

1. Pump 50 gallons of wastewater into a 55 gallon drum.

2. Add 300 ml of Alum followed by 150 ml of Sodium Hydroxide solution, then add 25 ml of an anionic polymer. Mix rapidly for 2 minutes with a variable speed motor mounted on the drum. Reduce the mixer speed to slowly stir the contents at about 30 rpm for about 10 minutes. Turn off the mixer. If wastewater contains paraquat or diquat bentonite clay should be added before the alum is added. About 1 liter of clay should be added to 50 gallons of wastewater.

3. Allow the solids in the drum to settle to the bottom. This should take place in 30 minutes to 1 hour. The supernatant in the tank should be discolored but transluscent. If you cannot see through a glass full of the supernatant you should add 200 ml of the Calcium Chloride solution and repeat step 2.

4. Pump the transluscent supernatant from the 55 gallon drum through the activated carbon columns. The carbon columns can be made by

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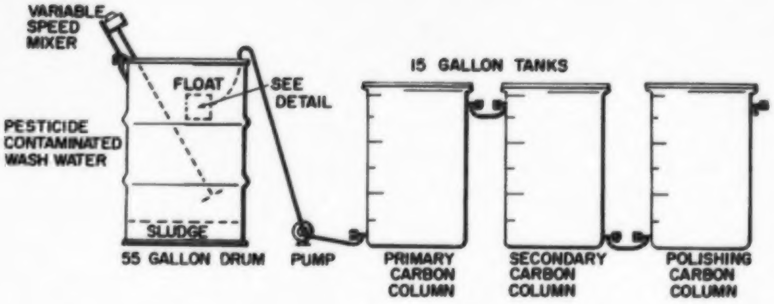
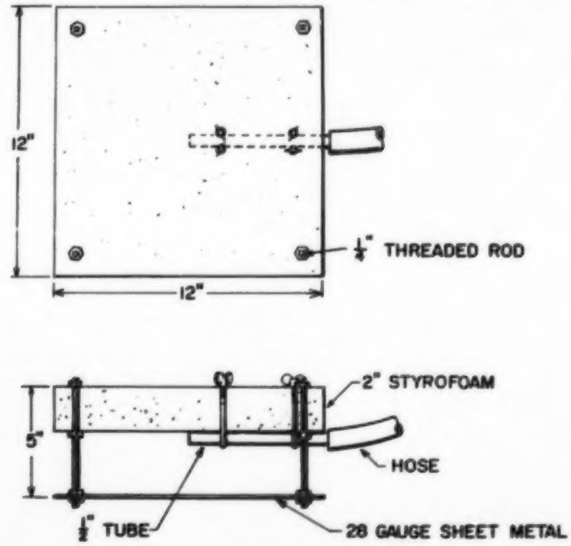

VARIABLE SPEED MIXER
FLOAT
SEE DETAIL
15 GALLON TANKS
PESTICIDE CONTAMINATED WASH WATER
SLUDGE
55 GALLON DRUM
PUMP
PRIMARY CARBON COLUMN
SECONDARY CARBON COLUMN
POLISHING CARBON COLUMN

Figure 19. Simplified system for treating pesticide contaminated wastewater.


12"
12"
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2" STYROFOAM
5"
HOSE
½" TUBE
28 GAUGE SHEET METAL

Figure 20. Detail dimensions of float for treatment system.

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putting 60 lb. of activated carbon in a 15 gallon drum. Spigots can be placed in the top and bottom and apposite side as shown in Figure 19. The flow can be controlled by the spigot on the first tank to reduce the flow to about .5 gal/min.

5. The effluent from the carbon column can be sprayed on grass or placed in a container and used to wash the application equipment.

B. Procedure for Preparing Chemicals to be used to Treat Wastewater

Sodium Hydroxide (3N)
Slowly add 5 lb of Sodium Hydroxide to 5 gallons of water in 5 gallon LPE Carboy. Caution: This solution will become very warm when mixed. Small amounts of Sodium Hydroxide pellets should be added periodically and allowed to dissolve. It will take about 1 hour to prepare this solution.

Aluminum Sulfate (Alum)
Add 5 lb of Aluminum Sulfate to 5 gallons of water in 5 gallon LPE Carboy. It is necessary to vigorously mix this solution for several minutes.

Calcium Chloride
Add 5 lb of Calcium Chloride to 5 gallons of water in 5 gallon LPE Carboy.

C. Chemicals (Amounts are based on treating 15000 gallons of wash water, about 2 years for the typical ag applicator.)

Aluminum Sulfate (Alum) Cat. No. 598-11652* 2 - 5 lb bottles @ $40.00	$ 80.00
Calcium Chloride Cat. No. 68-19302* 1 - 5 lb bottle @ $48.00	$ 48.00
Sodium Hydroxide Cat. No. 630-67802* 1 - 5 lb bottle @ $17.00	$ 17.00

*Catalogue numbers refer to:

G. Frederick Smith Chemical Co.
867 McKinley Ave.
Columbus, OH 43223
614-224-5343

Bentonite Clay

Volclay HPM-20
American Colloid Company
5100 Suffield Court
Skokie, IL 60076
312-966-5720

No endorsement of these companies is intended. Any chemical supplier can supply these products. You should check with local supply for best price and service.

Activated Carbon (115 lb @ $0.70/lb) $130.00

Filtrasorb 300 or Nuchar WVG

Calgon Corporation
Environmental System Div.
Filtrasorb Department
P. O. Box 1346
Pittsburg, PA 15230
412-923-2345

Westavco Chemical Div.
Carbon Department
Covington, VA 24426
703-962-1121

Anionic Polymer (Watcon 1255) or equivalent

15 gal @ $3.85/gal $ 57.75

Watcon, Inc.
2215 S. Main St.
South Bend, IN 48613
219-287-3397

Total Chemicals $332.75

D. Equipment

1. Tank for flocculation/sedimentation

   A. 55 gallon drum (can use a pesticide shipping container)

   B. Mixer - air drive mixer with regulator - requires 1 HP air compressor with tank - or equivalent variable speed mixer.
      Cat. No. 4318-40*
      1 air drive mixer drum lip mounting $196.00
      Cat. No. 4318-49*
      1 regulator, filter and lubricator $ 77.00

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2. Pump - 1/12 HP Polyethylene centrifugal pump	
Cat. No. 7001*	$ 96.95
2 - Service Kits @ $3.65	
Cat. No. 7001-60*	$ 7.30
3. Activated Carbon Columns	
Cat. No. 6321-21* (15 gallon)	
3 - polyethylene tanks with spigot cover @ $46.00	$138.00
Cat. No. 6314-20*	
3 - drain assembly kits @ $13.55	$ 40.65
Total Equipment	$555.60

E. Miscellaneous Supplies

Conical Graduates - 1000 ml	
Cat. No. 6135-45*	
2 - @ $7.45	$ 14.90
Rectangular Carboy with spigots (5 gallons)	
Cat. No. 6066-50	
3 - @ $32.02	$ 96.06
Total Miscellaneous	$110.96
Total Cost	$999.31

*Catalog numbers refer to:
Cole-Parmer Instrument Company
7425 North Oak Park Ave.
Chicago, IL 60648
800-323-4340

No endorsement of Cole Parmer is intended. Any supplier of such equipment, including local plumbing or hardware stores, should be considered.

F. Caution

When treating the wash water protective clothing should be worn. This material should be handled with the same precautions one would take in handling pesticides. The treatment unit can be housed in a small utility building to protect equipment from weather, but during operation the shelter should be opened to allow ventilation of the interior.

The carbon columns may support anaerobic bacterial growth. If the columns are not going to be used for several weeks the tanks holding the carbon should be drained. At the end of each year the first of the carbon columns should be emptied and refilled with new carbon. The column with new carbon should be moved to the polishing column position, the polishing column should be moved to the 2nd column position and the 2nd column should be moved to the primary position.

The flocculation/sedimentation tank will accumulate sludge during successive treatments. The sludge should be allowed to build up in the tank until the settled sludge reaches about 1/4 the height of the tank. In other words, for a 55 gallon drum settled sludge should be removed from the tank when the sludge blanket reaches a height of 10 inches. A floating intake to the pump would be used to remove the supernatant from the tank. This float can be made as shown in Figure 20. It is important to support the inlet to the pump about 2 inches above the sludge blanket. A piece of flat sheet metal will keep the float from settling into the sludge.

When the sludge blanket in the bottom of the tank reaches a depth of 10 inches, you should remove about half the sludge and store the waste in suitable containers such as those used to ship pesticides. Current research into techniques to encapsulate the sludge is underway.

Currently both the sludge and the used activated carbon would be considered hazardous waste. These types of waste can be disposed of by contracting with a hazardous waste disposal facility to remove the waste from your site.

If you produce more than 50 gallons of wastewater when you clean your equipment you may want to purchase a larger tank for the flocculation/sedimentation tank. These are available from various sources. A schematic of a larger treatment plant is shown in Figure 21.

G. Collection of Wastewater

Of course, before the treatment system can be used a means of collecting the wastewater must be developed. Figure 22 illustrates a modification that could be made in an existing concrete pad. The wash water was diverted to one corner by nailing 2x4 to the concrete pad with a nail gun and constructing a sump in one corner. The wastewater can be pumped from the sump into any type of above ground tank, or an underground tank could be located adjacent to the pad and the wash water diverted to the tank.

If you do not have an existing concrete pad and you may want to build a slightly more elaborate facility as shown in Figures 5 and 6. The volume of wastewater can be greatly reduced by covering the pad. Either a vinyl cover can be rolled over the pad when not in use or a building can be constructed over the washing pad as shown in Figures 6 and 7. This building could be used for pesticide equipment storage and would provide an all weather working environment for storing and maintaining your equipment.

Summary

The system described in this article will remove pesticides from wastewater. It is very important that the receipe presented is followed closely. The major cost of the treatment will be the disposal of the cost. Commercial facilities for such disposal are limited. Before constructing the washing station or purchasing the treatment system, you should contact your state pesticide office and the solid waste disposal authorities so that a practical plan can be used to dispose of the sludge. The volume of sludge that will have to be handled is variable but you can expect to have 15 to 30 gallons of sludge for each 1000 gallons of wastewater that you treat.

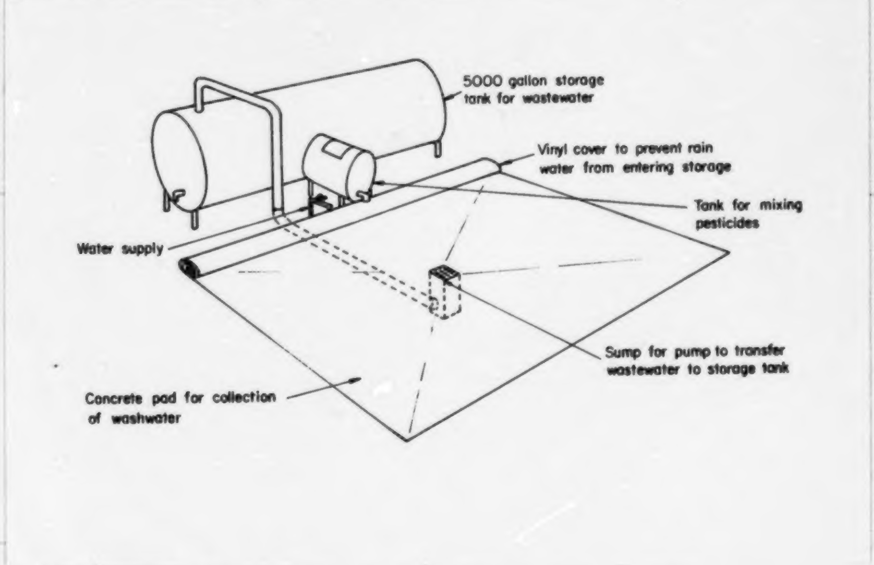
5000 gallon storage tank for wastewater
Vinyl cover to prevent rain water from entering storage
Tank for mixing pesticides
Water supply
Sump for pump to transfer wastewater to storage tank
Concrete pad for collection of washwater

Figure 21. Collection of pesticide contaminated wastewater in above ground tank.

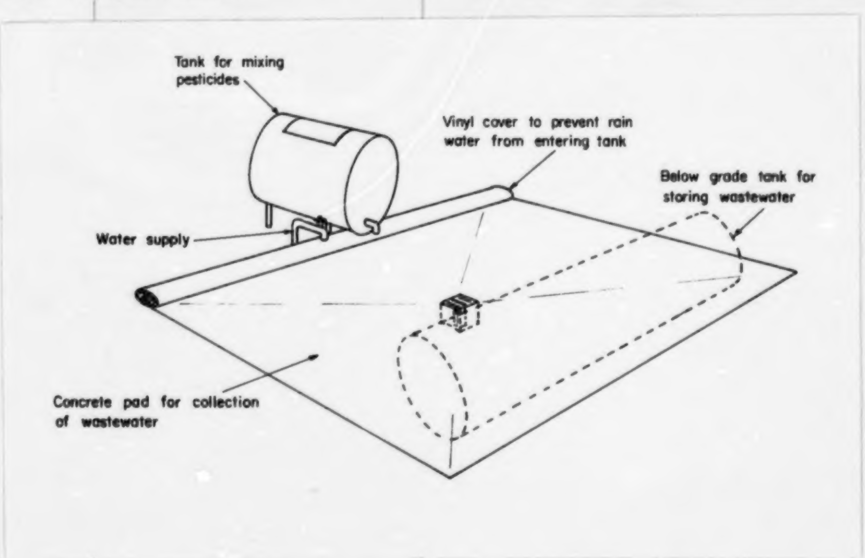
Tank for mixing pesticides
Vinyl cover to prevent rain water from entering tank
Below grade tank for storing wastewater
Water supply
Concrete pad for collection of wastewater

Figure 22. Collection of pesticide contaminated wastewater in below ground tank.

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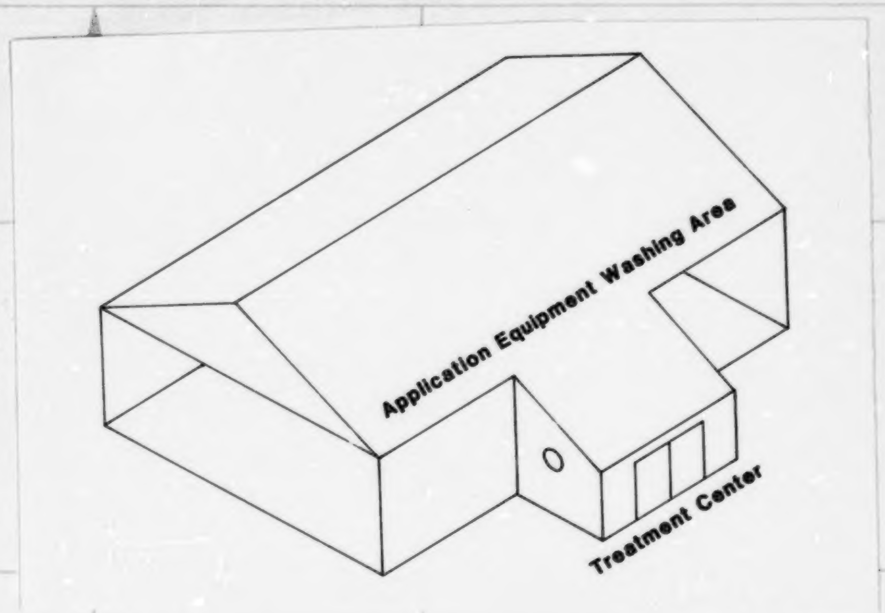
Application Equipment Washing Area
Treatment Center

Figure 23. Pesticide wastewater control system.

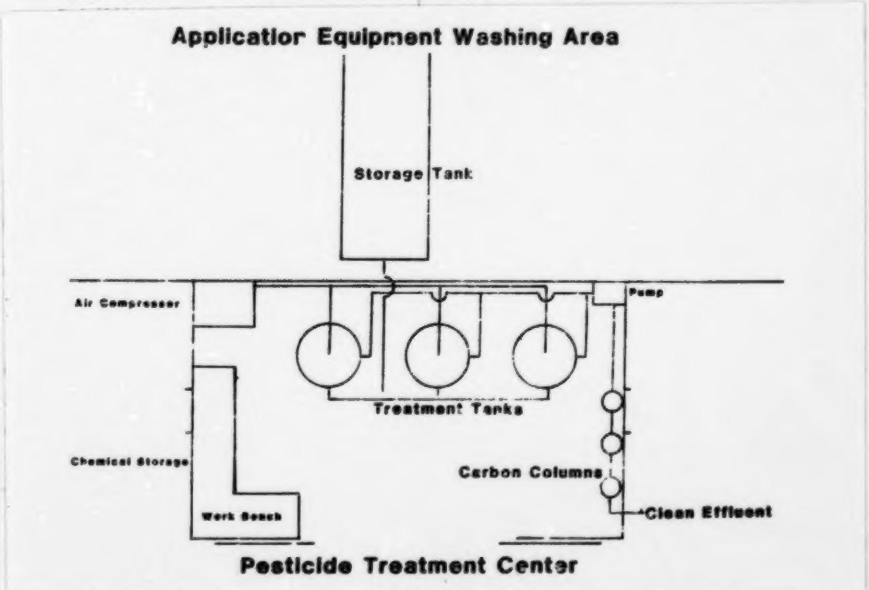
Application Equipment Washing Area
Storage Tank
Air Compressor
Pump
Treatment Tanks
Chemical Storage
Carbon Columns
Clean Effluent
Work Bench
Pesticide Treatment Center

Figure 24. Pesticide wastewater treatment center.

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